Montana Department of
ENVIRONMENTAL QUALITY

MEMO

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To: Mindy McCarthy, Water Quality Planning Bureau QA Officer, and other members of the Water Quality Planning Bureau

CC: Eric Urban, Water Quality Standards Section Supervisor; Michael and Sandra Head, Precision Measurement Engineering, Inc.

From: Michael Suplee and Rosie Sada, Water Quality Standards Section

Date: November 14, 2014

RE: ***Technical Memorandum*: Best use of MiniDOT Loggers for Dissolved Oxygen Measurement in Streams and Rivers, Part 3**

Introduction and Purpose

This technical memorandum (Part 3) is a continuation of a series of evaluations of MiniDOT dissolved oxygen/temperature sensors. These evaluations have been undertaken on MiniDOTs equipped both with and without anti-fouling devices (see the Part 1 technical memo dated December 5, 2011 and the Part 2 memo dated May 13, 2013). The purpose of the present memo is to provide our evaluation of an improved anti-fouling device (a coarse-mesh copper screen) provided by Precision Measurement Engineering, Inc. (PME). We tested the coarse copper screens in 2013 and 2014. Our earlier tests showed that, over an extended time period, slack water sites (i.e., those with no flow) where high attached algal/biofilm growth can be expected are the most difficult locations for the MiniDOT to maintain high-quality data in. Therefore, this memo addresses instrument comparisons conducted in slack water sites.

Methods

In fall 2013, a MiniDOT logger was deployed side-by-side with a YSI 6600 V2-4 sonde which had an optical DO sensor and wiper (wiping interval: 15 min). Total deployment was 23 days. Initially, the MiniDOT had no anti-fouling deterrent at all; but after eight days deployment, the MiniDOT was retrieved, cleaned, and equipped with a coarse-mesh copper screen (**Figure 1**)[1]. The deployments occurred at a slack water site (i.e., no flow) where biofilm growth was expected to be substantial, as part of a planned research monitoring project in Eastern Montana. The YSI and MiniDOT were each attached to a fencepost pounded into the

[1] PME developed the coarse-mesh screen partly in response to the less-than-satisfactory results from the previously tested passive anti-fouling devices (see Memo 2, dated 5/13/2013).

stream bottom, and their sensor faces were situated at the same depth (ca. 0.5 m below the surface). The MiniDOT was mounted horizontally.

In 2014, another MiniDOT equipped with a coarse copper screen was deployed alongside a YSI 6600 V2-4 with an optical DO sensor and wiper (wiping interval: 15 min). The 2014 site was also a slack water site in Eastern Montana, but the deployment was more than twice as long (48 days). Biofilm growth was also expected to be high. Similar to the 2013 site, the instruments were mounted on a fencepost (and again, the MiniDOT was mounted horizontally). However, the MiniDOT was located approximately 8 cm closer to the water surface due to deployment difficulties (the water was too deep for the waders!).

Figure 1. MiniDOT logger equipped with a coarse-mesh copper screen, which acts as a passive anti-fouling device.

For each YSI-MiniDOT pair, performance was compared by calculating three DO values important for DEQ's stream assessment: the daily DO maximum, the daily DO minimum, and the daily delta (daily maximum — daily minimum). In addition, for each daily dataset, the difference (expressed as a percent) between the YSI and the MiniDOT DO observations were calculated as follows:

<u>Daily DO Delta</u>

% Difference = **([**YSI MAX (mg DO/L) – YSI MIN (mg DO/L)**]** – **[**MiniDOT MAX (mg DO/L) – MiniDOT MIN (mg DO/L)**])** ÷ (YSI MAX (mg DO/L) – YSI MIN (mg DO/L)) (1)

<u>Daily DO Minimum or Maximum</u>

% Difference = [YSI MIN (mg DO/L) – MiniDOT MIN (mg DO/L)] ÷ [YSI MIN (mg DO/L] (2)

Note: The daily minimum values are replaced with daily maximum values in equation 2 to get the daily maximum % difference.

In all cases the YSI data had passed DEQ's *a posteriori* QC for allowable drift from calibration, instrument interference by snagged drifting algae, etc., and were considered reliable readings. Therefore, the YSI observations are in the denominator of the % difference equations (as opposed to using the average of the YSI and MiniDOT observations).

Results: 2013 Slack Water Site

When the two instruments were retrieved from the 2013 slack-water site, no filamentous algae were snagged on either one. Field notes state that, upon retrieval, "the copper screen on the MiniDOT appears to be working. The MiniDOT body had a thin coating of algal film all over it but under the Cu screen the probe face looked very clean." All the wipers on the YSI were working properly. **Figure 2** shows the post-QCed, side-by-side DO record from the two instruments, both before and after the installation of the copper screen.

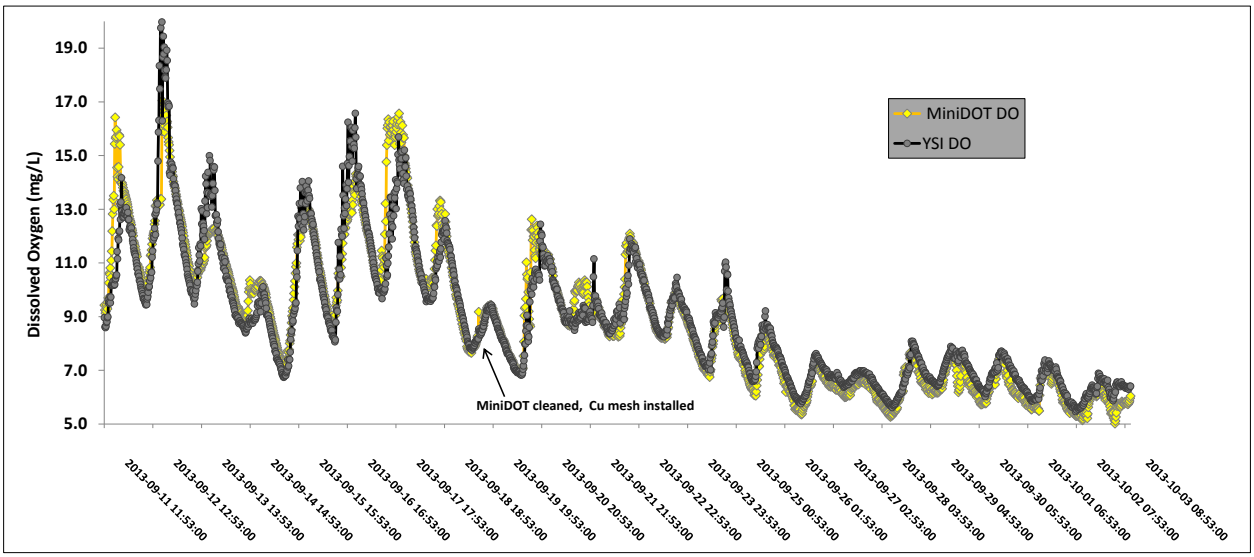

Figure 2. Complete DO Record for the YSI and MiniDOT at the 2013 Slack-water Site, Before and After the Installation of the Coarse Copper Screen on the MiniDOT.

Figure 3 shows the daily DO delta, daily DO maximum, and daily DO minimum as measured by both instruments, both before and after the copper screen was installed on the MiniDOT. **Figure 3A** shows that there was often substantial disparity between the daily DO deltas of the two instruments during the first eight days, when the MiniDOT had no anti-fouling device. However, following cleaning and installation of the coarse copper screen, the instruments' DO deltas are nearly identical, with a single exception on 9/24/2013. In the pre copper-screen period, the absolute % difference[2] in DO deltas between the instruments averaged 20.3% whereas in the post copper-screen period, it averaged 8.1% (**Figure 4**).

[2] Absolute difference means that all values generated by equation 1 (% difference in DO delta) were converted to their absolute values prior to computing a dataset average.

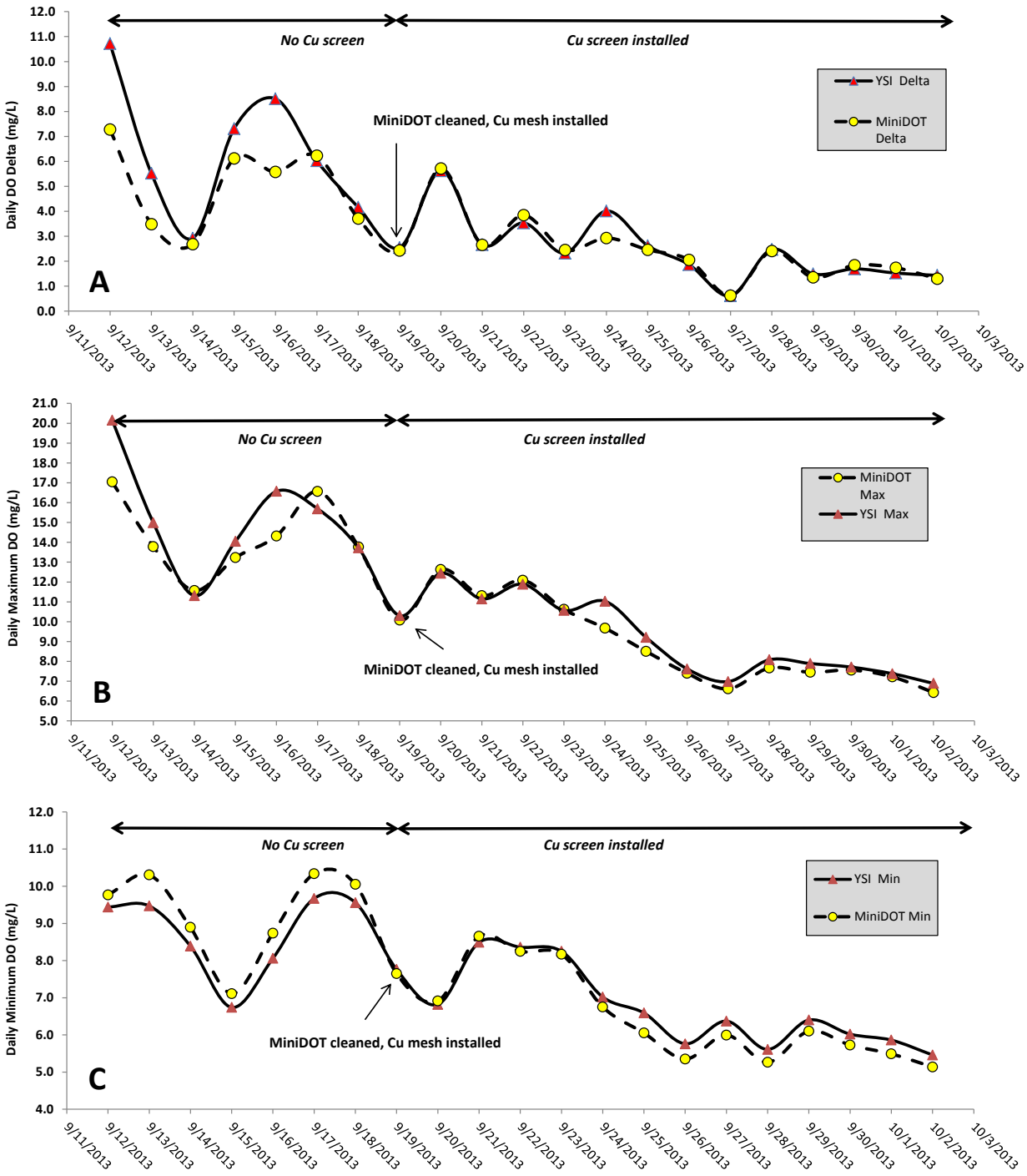

Figure 3. Time series plots of YSI and MiniDOT Dissolved Oxygen Recordings from the 2013 Slack-water Site. (A) Daily DO delta. (B) Daily DO maximum. (C) Daily DO minimum. The MiniDOT had no copper screen for the first eight days, but was equipped with a coarse copper mesh for the remaining 13 days of deployment. Only data for complete days are shown (data for partial days at the start and end are excluded).

There was some initial trending in the percent difference between the instruments' minimums and maximums in the days following the installation of the copper screen (**Figures 3B, 3C**). Essentially, the MiniDOT's daily DO minimums became increasingly lower than the YSI's over the first six days or so, after which the differences stabilized at about 6%. Simultaneously, the MiniDOT's daily *maximums* became increasingly lower than the YSI's over the same time period, and then stabilized at about a 5% difference (**Figure 3B**). These effects cancelled one another and as a result, the daily DO deltas provided by the two instruments remained very close (**Figure 3A**).

There is no systematic departure (trend) evident between the two instruments' DO deltas over the 13 days between 9/19/2013 (installation of copper screen) and retrieval on 10/3/2013 (**Figure 3A, Figure 4**). The Durbin-Watson test (Ott, 1993) was used to test for serial correlation in the % difference[3] time-series data in **Figure 4**, post-installation of the copper screen; the test would indicate if a systematic drift in MiniDOT DO deltas (relative to YSI deltas) was occurring over time. The Durbin-Watson value was 2.01, indicating that there was no serial correlation (i.e., no positive or negative trending). Thus, an important characteristic of **Figure 4** is that the % differences in DO delta between the two instruments did not show a clear trend after the copper screen was installed; rather, the differences oscillated around a 0% difference, with an average difference (absolute) of 8.1%. This is a substantial improvement from earlier anti-fouling devices we tested in slack water; the earlier anti-fouling devices only provided good data collection for about 5 days, essentially the same as MiniDOTs with no anti-fouling device at all (see Memo 2 of this series).

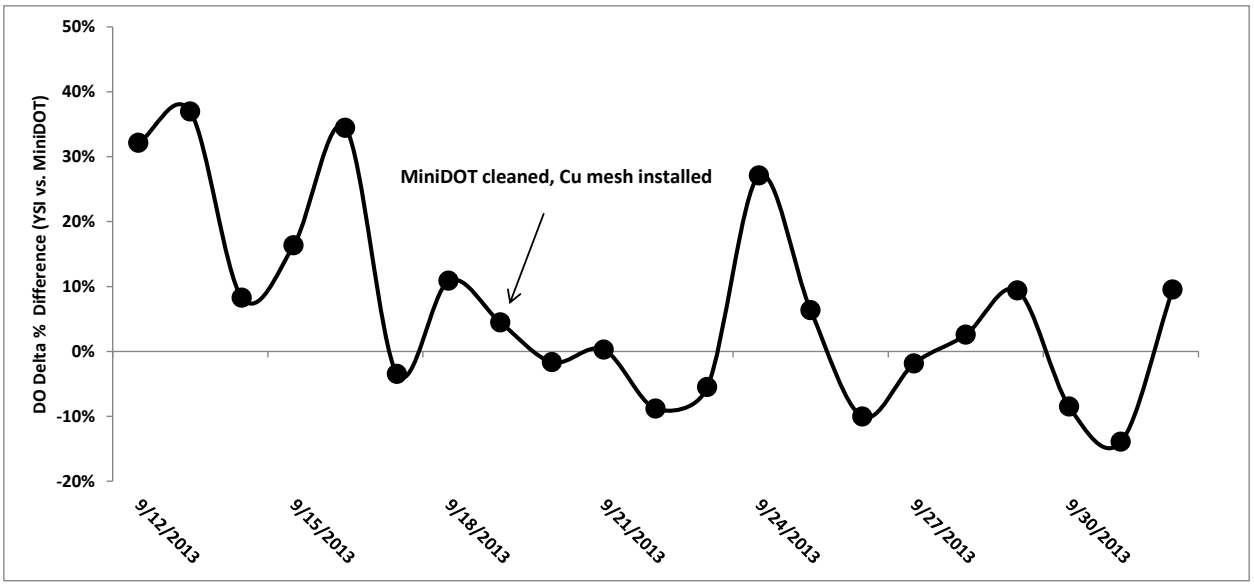

Figure 4. Percent Difference in DO Deltas between the YSI and MiniDOT at the 2013 Slack-water Site.

[3] The Durbin-Watson test was applied to the % difference data that were not absolute (i.e., the same values as shown in **Figure 4**).

Results: Slack Water Site-2014

Figure 5 shows the post-QCed, side-by-side DO record from the two instruments. Field notes recorded at the time of their retrieval (October 3rd) indicated that all the YSI wipers were working fine, and that the MiniDOT's copper screen had been helping to prevent growth of algae on the sensor face.

Overall, the two instruments tracked one another well over an extended period, which is in sharp contrast to what we observed when a MiniDOT had no anti-fouling device (see Figure 1 of Memo 1).

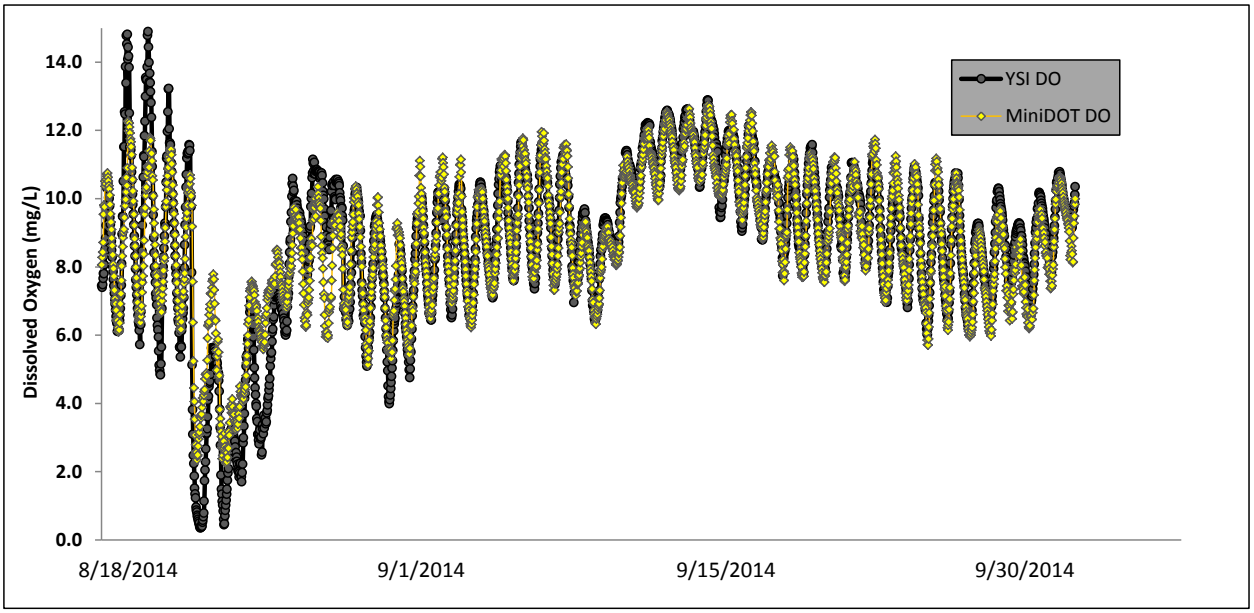

Figure 5. Complete DO Record for the YSI and MiniDOT at the 2014 Slack-water Site. Values shown are the 30-minute averages of each instrument, because in this case, they collected data on different time steps (the YSI every 15 min, the MiniDOT, every 10 min).

Initially there were large discrepancies between the two instruments DO deltas (**Figure 6A**), but within five days this diminished and thereafter the deltas were similar most of the time. The large differences in deltas following initial deployment were driven by the fact that the YSI recorded higher highs and lower lows that the MiniDOT (**Figures 5, 6A,** and **6B**). In terms of decision making relative to the DO delta of 5.3 currently in use in DEQ's assessment methodology (Suplee and Sada de Suplee, 2011), the YSI data indicated exceedences on seven occasions, the MiniDOT on six (**Figure 5A**). DO deltas greater than the benchmark value of 5.3 corresponded between the two instruments on five of those occasions, although their actual values differed.

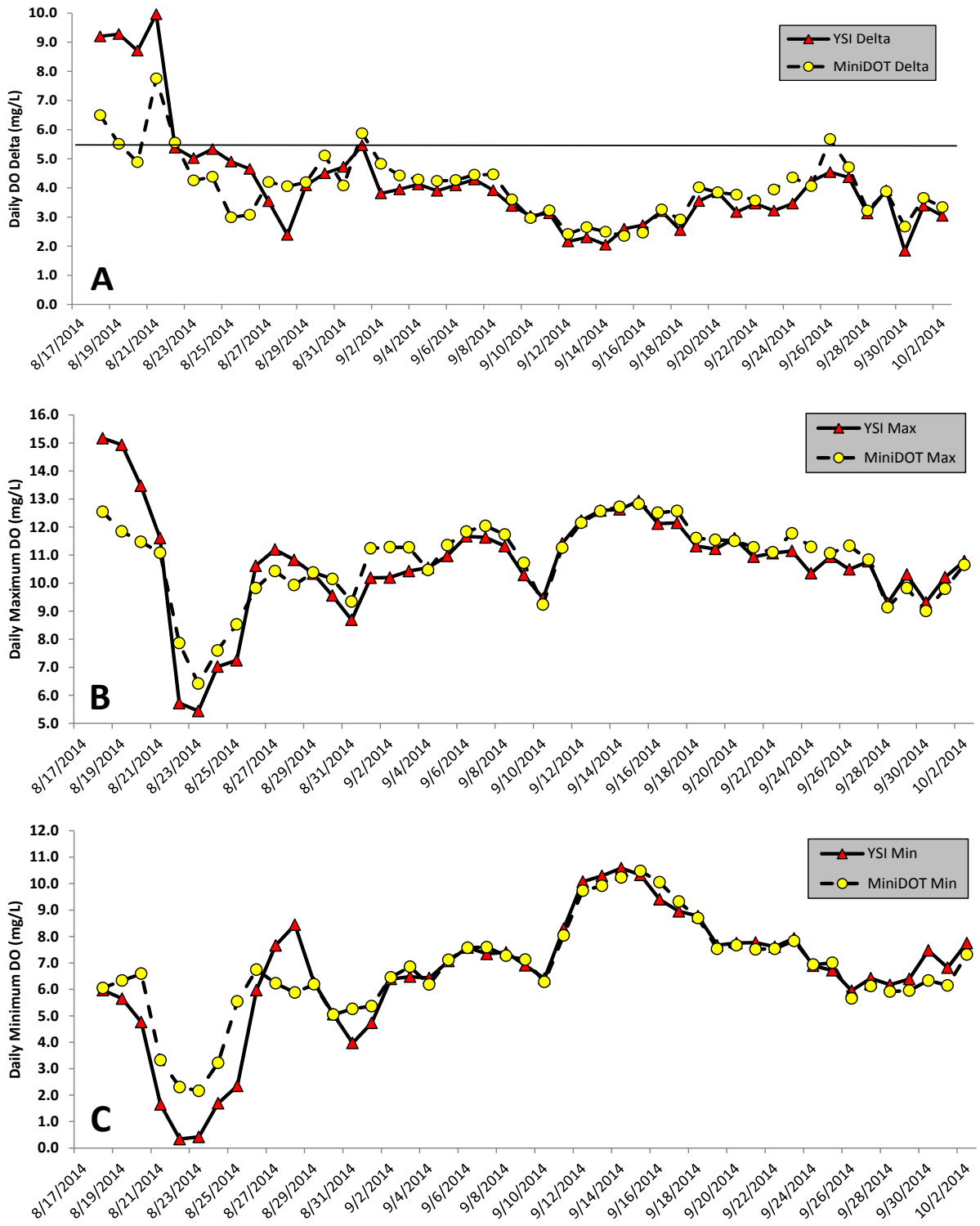

Figure 6. Time series plots of YSI and MiniDOT Dissolved Oxygen Recordings from the 2014 Slack-water Site. (A) Daily DO delta. (B) Daily DO maximum. (C) Daily DO minimum. Only data for complete days are shown (data for partial days at the start and end are excluded). The black horizontal line in (A) is the currently-used decision threshold for DO delta.

Temporal trending in the MiniDOT's DO delta was evident—but weak—over the 48 days of deployment (**Figure 7**), and was driven primarily by the data from the first days of deployment. In the first ten days after deployment, the % difference between the two instruments' DO deltas was high and erratic, after which (from 8/29 onward) it became less variable and averaged 11.3% (absolute). For the entire time series, the Durbin-Watson statistic was 1.4, indicating weak serial correlation (i.e., trending) for the entire period. If only the 35-day period from 8/29 onward is analyzed, the Durbin-Watson statistic is 2.3, indicating no serial correlation (and thus no trending). So, for 35 days—beginning well after the point in time when biofilm typically causes problems in MiniDOT DO measurement (i.e., 5 days post-deployment)—the MiniDOT's DO deltas showed no systematic drift from the YSI's.

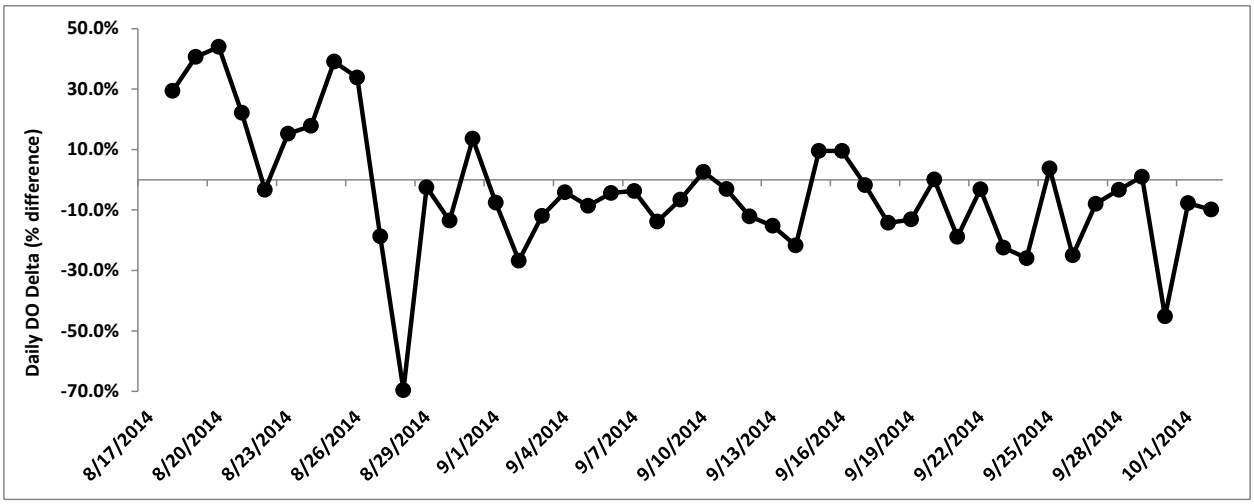

Figure 7. Percent Difference between DO Delta values from the YSI and MiniDOT at the 2014 Slack-water Site.

Discussion

In slack-water deployments we have carried out before, using earlier, prototype anti-fouling devices, MiniDOT DO delta values steadily departed from the corresponding YSI values across the entire deployment period (see Figure 6 of Memo 2). Consequently, we recommended in our last memo that MiniDOT sensors be cleaned every 5-7 days. In contrast, in the comparisons presented here where the MiniDOTs were equipped with a coarse copper screen, a systematically-increasing departure from the YSI data was absent, or only weak. In 2013, over the course of fifteen days after the MiniDOT was equipped with the copper screen, differences between the two instruments oscillated around 0% and averaged 8.3%[4] (**Figure 4**). During that period, the MiniDOT daily lows and highs were usually within about 5% of the YSI's (**Figures 3B and 3C**). In 2014, there was weak trending for the % difference in DO delta across the entire deployment period; the MiniDOT's DO deltas were initially lower than, but ended up being slightly higher than, the YSI's (**Figure 6A**). But for the last 35 days of the 2014 deployment, the MiniDOT deltas averaged an absolute difference of 11.3% from the YSI, and no significant trend in time was observed (**Figure 7**). For slack-water sites, 35 days represent the longest period of time we have observed MiniDOT readings to be consistent with the simultaneously-deployed YSI.

[4] This average (8.3%) is of the absolute values.

The disparity in DO deltas in the first few days after deployment (**Figure 6A**) is not readily explicable. Too little time has elapsed to suspect biofilm interference, and besides, data from later in the series indicate biofilm interference was negligible. In another MiniDOT-YSI side-by-side comparison in flowing water (data not shown), we again noticed DO reading disparity at the start of the deployment, but after a few days the instruments provided very similar results. Our tests in 2012 (see Figure 3 in Memo 2) also showed a short-term effect of sensor cleaning on the MiniDOT's data. Thus, it may be best to leave the MiniDOTs in place a few days or so to get the best results.

Assuming that a 10% departure from YSI DO deltas is acceptable, the 2013 and 2014 data signify that the coarse copper screen anti-fouling device allows the MiniDOT to provide acceptable data over long deployments (up to a month and a half) without strong, systematic bias. The 2013 and 2014 results also show that daily DO deltas computed from MiniDOT data are often somewhat higher (> magnitude) than the corresponding values recorded by the YSI (**Figures 3A, 6A)**, though frequent exceptions exist. As can be seen in the DO concentration data (**Figures 2, 5)**, the two instruments tracked one another very well, but did not, on a day-to-day basis, always provide exactly comparable results. As a result, computed DO deltas can be sharply different in some cases (August 19th in **Figure 6A**, for example).

Conclusions and Recommendations

1. Among the passive anti-fouling devices we have so far tested on the MiniDOT, the coarse copper screen has shown the best capability of providing good-quality DO data over time. Good DO data were obtained for over a month and a half of deployment, with no interim cleaning events, with little or no systematic drift from true (as benchmarked by YSI 6600 data) DO concentrations. Equipped with the coarse copper screen, DO delta values measured by the MiniDOT can be expected to be, on average, ±10% of values measured by a YSI 6600 with wipers. However, you can expect that there will be individual results (days) which will differ by substantially more than 10% from what would have been measured using a YSI.

2. Careful observation and recording of the condition of the MiniDOT's sensor underneath the coarse copper screen should always be made upon retrieval. We have deployed MiniDOTs at dozens of slack-water sites and in most cases the coarse copper mesh clearly deterred algal growth, but there were exceptions. Fine mud can also build up and partially cover the sensor. Your recorded observations will help immensely back in the office, when the veracity of the data is evaluated.

3. In some instances MiniDOTs appear to demonstrate a "settling in" period, lasting several days or longer, during which readings may be considerably different from the YSIs, compared to later in the deployment. This finding signifies that longer deployments (with a coarse copper mesh) may give the best indication of DO patterns at a site. We recommend no less than 5 days.

References

Ott, R. Lyman. 1993. An Introduction to Statistical Methods and Data Analysis - Fourth Edition, Belmont, CA: Duxbury Press.

Suplee, Michael W. and Rosie Sada de Suplee. 2011. Assessment Methodology for Determining Wadeable Stream Impairment Due to Excess Nitrogen and Phosphorus Levels. Helena, MT: Montana Department of Environmental Quality Water Quality Planning Bureau. WQPMASTR-01.