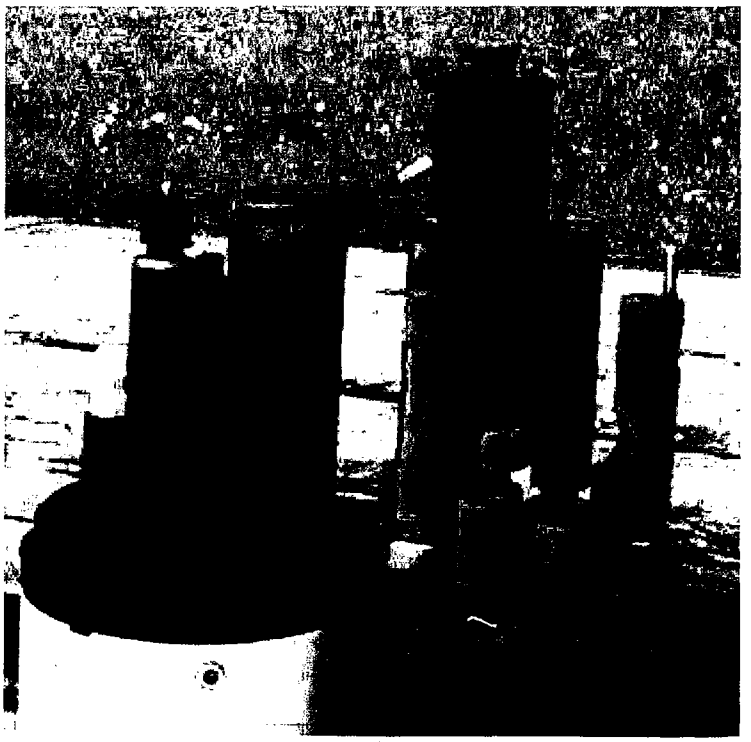
COMPARISON OF TWO MULTIPARAMETER WATER-QUALITY SONDES AT BEAR CREEK NEAR SILVER HILL, ARKANSAS



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Produced by:

Faron D. Usrey

Buffalo National River

Resource Management, Water Division

INTRODUCTION

In the fall of 2001 the staff of Buffalo National River (BUFF) volunteered to participate in the Multiparameter Probe DEMO Project sponsored by NPS, Water Resources Division. The purpose of this demonstration of multiparameter sondes was to assess, compare, and contrast the various multiparameter water-quality instruments on the market to provide insight into future instrument procurements made by the Networks under the NPS Vital Signs Monitoring Program. In cooperation with the U. S. Geological Survey (USGS, Water Resources Division, Little Rock District), the staff of BUFF installed two multiparameter water-quality sondes at USGS's Bear Creek site.

In early October of 2001, BUFF and USGS met with representatives from Yellow Springs Incorporated (YSI) to install a multiparameter sonde (YSI Model 6600) unit at the Bear Creek site. The unit was linked to a Data Collection Platform (DCP) that used a satellite radio transmitter to broadcast hourly stream condition data to the USGS office in Little Rock, AR. Later that month, a representative from the Hydrolab Corporation consulted with BUFF and a Hydrolab (DataSonde 4a) was linked into the same system. Parameter graphs for both sondes were posted on the USGS, Arkansas District website (http://arkweb.er.usgs.gov) for the duration of the comparison study, and results could be viewed either in a graphical format or downloaded as raw data. These units collected data for six months. Chronological disruptions in data collection were rare and only two disruptions were experienced. One was an error in sonde program setup selection, and the other was due to a damaged probe. None of the disruptions were a result of faulty equipment. Both units performed to specifications for the entire duration of the comparison and no problems in maintenance were experienced.

SITE DESCRIPTION

Bear Creek is a large tributary of the Buffalo River, and has been monitored by the USGS at the current location near Silver Hill, Arkansas (07056515) since January 1999. Bear Creek has a drainage area of 83.1 square miles and is primarily situated in Searcy County. Bear Creek flows northeasterly through two geologic provinces, the Boston Mountains and the Springfield Plateau, and unites with the Buffalo River approximately 1 river mile below the town of Gilbert, Arkansas. The unit installation was below the new Highway 65 bridge in the state right-of-way (Lat 35°57'00", Long 92°43'30"), (Figure 1).

TYPES OF SONDES USED IN BUFF DEMO

The YSI Model 6600 (http://www.ysi.com) was the first sonde to be deployed at Bear Creek, October 2nd, 2001 (Figure 2 and 3). This extended deployment sonde had self-contained software with the following probe configuration; non-stirring Rapid Pulse™ dissolved oxygen system, antifouling/wiped turbidity probe, specific conductivity, pH, and temperature. The Model 6600 required a 30-second warm-up for sensor polarization.

The next sonde to be installed was the Hydrolab DataSonde 4a, October 16th, 2001 (Figure 2 and 3). This long-term deployment sonde was self-contained (http://hydrolab.com) and featured the shuttered turbidity sensor, pH, dissolved oxygen sensor with magnetically driven stirrer, specific conductivity, and temperature. The DataSonde 4a required a two-minute warm-up time, and the DO probe required a mechanical stirrer. New models for both YSI and Hydrolab are now on the market and improvements in the turbidity and dissolved oxygen sensors may make some of the information garnered in this study obsolete.

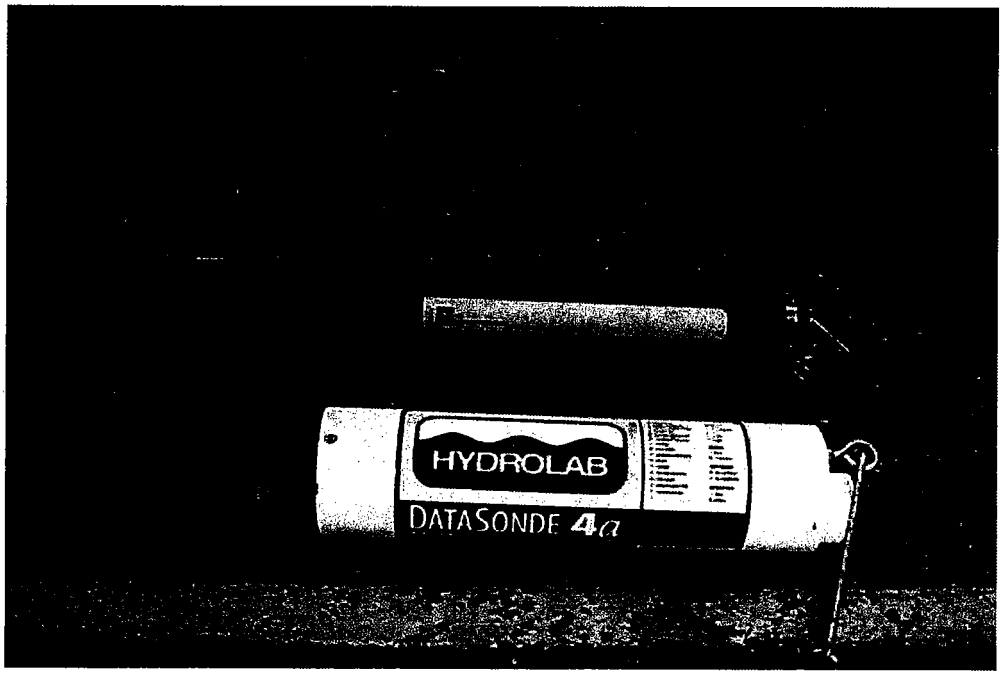


Figure 2. YSI Model 6600 (at top) with the Hydrolab DataSonde 4a.

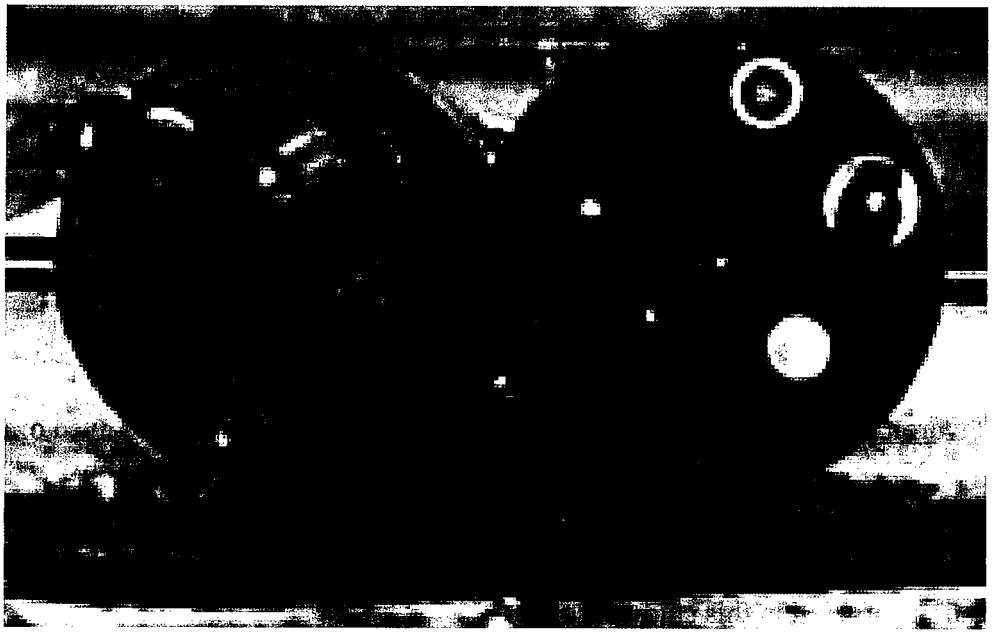


Figure 3. YSI Model 6600 (at left) and Hydrolab DataSonde 4a, probe presentation. The Hydrolab is outfitted with a mechanical stirrer adjacent to the dissolved oxygen meter (top right probes). Both units have shutter wiped turbidity probes.

DATA COLLECTION

Sonde units were both capable of taking discrete and unattended samples. Discrete samples are those prompted by an operator using hardware such as computer or handheld data logger that is in direct control of the sonde. Unattended samples are those in which the sonde is preprogrammed and functions independently from the operator. Unattended sampling can have software directly connected or disconnected from the sonde. Two types of unattended samples were used in this project.

The first type of unattended sampling used the setup software contained within the sonde. Using a PC based software, which both companies provided; the sondes were programmed to collect data every 15 minutes. In order to do this, the sondes were connected to a PC and sampling parameters were defined and stored in the software within the sonde. This process typically took less than 15 minutes. Once the parameters and duration of sampling were defined, the sonde was disconnected from the PC and then deployed. Once deployed, the sonde would awaken every fifteen minutes, warm-up, and sample. Data were stored internally, and could be retrieved at the end of the deployment cycle. Sondes used in this study were connected to the gauge house by a data cable, but deployment for both of the sondes could have been done without any cable connections, the sondes were totally self-contained.

The second type of unattended sampling was using a DCP to prompt the sondes to sample. Setup by USGS (Arkansas District), the DCP requested a sample from each of the sondes each hour using a common programming language called SDI12 (Serial/Digital Interface at 1200 baud). SDI12 is a language that is common to most hydrologic sensors that are used to measure long-term, insitu measurements; such sensors include pressure transducers, hydroacoustic meters, and water-quality sondes. Once time for the sample collection, the DCP would signal the sondes that a sample was required, and the sondes would begin a warm up protocol (30 seconds to 2 minutes depending upon the sonde type). Once sufficiently warm, the DCP would prompt the sondes for an unattended sample and each sonde would respond in succinct order for the following parameters: temperature, dissolved oxygen, percent dissolved oxygen, specific conductivity, pH, and turbidity. These coded measurements would be stored within the DCP until a transmit time was reached (Greenwich Time). These hourly USGS collections were independent of the 15-minute interval collections programmed by BUFF staff. For example, each sonde was programmed to collect and store data every 15 minutes for the purposes of the NPS comparison project. However, on the hour they would be prompted by USGS's DCP for a parameter suite reading. When both the DCP and the programmed 15 minutes sampled were requested at the same time, the sondes would process the requests in sequence with no loss of data.

INSTRUMENT CALIBRATION

Calibration techniques for both sondes were similar, and differences were based upon the sonde interfacing software. Both companies provided interfacing software that was of high quality and user-friendly. During sonde programming, sondes used a DOS type prompt that required number selections to negotiate the calibration steps. Hydrolab's calibration techniques were simpler and reduced the amount of information needed to calibrate individual probes and calibration documentation. This was beneficial, but simplicity gained, meant that troubleshooting an individual probe was less effective. For instance, in order to calibrate the pH probe on the Hydrolab, no extra diagnostic selections were necessary in the calibration process; simply put the standard in the calibration cup and accept the probes reading on the calibration standard. However, on the YSI it was recommended to select two or three diagnostic profilers such as the millivolt output of the probe. This additional step took longer to perform and was more tedious to document, but the information gained would notify the user when a probe was starting to corrupt and exceed the calibration range. This was beneficial because when a probe exhibited warning signs, another probe could be obtained before the probe actually began to lose data. This procedure was useful, but consistently documenting all the recommended diagnostic profilers for all of the probes can be frustrating during the learning curve phase after initial installation.

Standards are expensive, especially the turbidity standards. Sonde calibration requires a high volume of standards to achieve a quality calibration. During the calibration process approximately 500 to 700-ml of each standard is needed; pH (7 and 10), specific conductivity, and turbidity standards are all needed to calibrate each sonde. Turbidity standards typically cost around $100 per liter. Specific conductance and pH range between $20 to $28 per liter. However, short cuts in the volume of standard used can be made without compromising the quality of the probe calibration. For instance, saving the old pH standard in a separate bottle to be used as a pre-rinse for the next calibration can save approximately 400-ml of standard per calibration. This is acceptable as long as attention is given to removing the entire old standard before dispensing the fresh standard for the final calibration step. Another money saving technique is to buy a concentrated turbidity standard and dilute the standard to the 100 NTU, which is required by both manufacturers. A formazin turbidity standard can be acquired from several chemical manufactures. Simply take the concentrated standard (typically 4,000 NTU) and run the concentrated standard through a dilution series down to 100 NTU. Caution should be taken to use precise dilution techniques and to check the end product against a known 100 NTU standard. BUFF used a lab grade turbidity meter to check the end product standard against a known 100 NTU standard. Concentrations slightly over 100 NTUs could be further diluted down to 100 NTUs by using the meter to fine-tune the concentration. Concentrations under 100 NTUs were thrown out and not used to calibrate the sondes. Department of Interior agencies can order most standards through the USGS's Ocala Laboratories at discount (see http://1stop.usgs.gov or ocalaman@usgs.gov).

OPERATIONAL PROBLEMS

Once practiced, a calibration session for each sonde unit averaged 30 minutes. Approximately, 80% of the calibration trips were accomplished streamside, and due to poor weather, (rain or extreme cold) the rest of the calibrations were made at a BUFF maintenance facility located 5 miles north of the installation. Each trip consisted of taking a precalibration measurement, downloading data, cleaning the sonde, calibration, reinstallation, and then a postcalibration environmental measurement.

Precalibration and postcalibration measurements were used to indicate errors in calibration and were supplemental in indicating probe drift. Any large differences between the pre and post measurements can indicate an error during the calibration process, and these measurements were needed as a backup security against collecting erroneous data during an extensive sonde deployment. Also the difference in the pre and post measurements was an indication of drift, but not an actual measurement. The true measurement of drift occurs during the calibration process. Pre and postcalibration environmental measurements are not absolute measurements of drift because diurnal changes in temperature produce predictable changes in the physicochemical properties in parameters where temperature is a common factor. Specific conductivity, dissolved oxygen, and pH are all directly affected by changes in temperature.

Calibration drift is the electronic drift in the probes from the first time it was calibrated to the present, and any differences between readings of a cleaned sensor in standards is considered drift (Wagner et al., 2000). In order to account for drift during the numerous comparison deployments, detailed calibration records were kept. As discussed earlier, the YSI had more diagnostic software selections to document, and was slightly more complicated to document in the initial portion of the calibration trips. However, these diagnostic tools were very helpful in explaining why individual probes may have drifted during the deployment. During the test comparisons of the selected sondes, dissolved oxygen was the most prone to drift. Sedimentation of the probes was the most frequent cause of drift in dissolved oxygen (DO), and the Hydrolab drifted most. The reason for this is based in the mechanical stirring device that is located near the DO probe (Figure 3). A pulsating magnet within the base of the stirrer drives the Hydrolab stirring unit. The alternate magnets in the blades would resist the pulsating magnets and the blades would turn on an axle located in the blade. Fine sediment, especially sediment containing iron fragments, would collect around the axle and the space between the countercurrent magnets. Eventually the iron fouling would lead to a mass of granular sediment that would stop the blades from turning. Once stopped, water flow across the DO membrane was reduced and a difference in the measurement of DO occurred. The YSI has a non-stirring Rapid Pulse™ dissolved oxygen system and can measure DO without a needing a constant flow over the membrane.

Steps for downloading data from the sonde to a PC were simple for both sonde types. The YSI interfacing software was Windows™ based and downloaded data was immediately graphed in the main window when downloading was complete. The

downloaded data from the YSI was available in graph form for printing or in a spreadsheet format. If the spreadsheet option was selected the data could simply be saved as an Excel™ file. Downloading of data for the Hydrolab was a more complex. File parameters had to be defined before the download could take place, and the transfer baud rate was quite low. The Hydrolab took nearly 3 times longer to download data than did the YSI. Once downloaded, the file was saved in a generic form, and could then be opened in Excel™. One problem during this conversion of data from one file type to another was that the date would not be accepted as an actual date in Excel. Converting the date from text would have to be done manually. Several approaches to solve this problem were attempted and finally the appropriate route was found. This problem could have been solely the product of the operator, but the problematic step did not exist in the YSI downloading process and therefore, did not lead to confusion.

Cleaning the sondes of sediment and algae buildup is a precarious and tedious process that could lead to probe damage if not done properly. Sediment buildup within the holding pipes did occur during storm events even though the pipes were positioned within the flowing portion of the stream during the entire comparison project. Sediment can fill in between the probes, clogging the measuring devices on the probes and potentially changing the redox potential of the aqueous environment around the sensors. Sediment was best removed during maintenance by using a spray bottle with an adjustable type nozzle. Both sondes came with brushes for cleaning the probes, but extreme care should be given while using the brushes. The slightest slip in pressure can send the brush bumping into sensitive parts of the probes, like the pH bulb or the dissolved oxygen membrane. The pH probe is the most sensitive and difficult to replace. During the initial phase of the comparison, a brush came into contact with the glass sphere and damaged the YSI pH probe, which resulted in a loss of data. Both of the sondes have probes that are interchangeable, and probe replacement can be done in the field. So, with good reason, it is recommended that an extra pH probe be available if continuous data collection is highly important to the investigation. Although biofouling was expected at the Bear Creek due to its increasing eutrophic condition, the deployment during the cooler seasons produced little biofouling of the probes. All of the probes were easily cleaned prior to calibration. With the exception of the damaged probe; no data was compromised or lost due to excess buildup on the probe sensors.

After the data was downloaded and the sondes recalibrated, the sondes were redeployed within the holding pipes. Since positioning within the stream cross-section is important for correct representation of the environmental conditions at the site, consistent positioning of the sondes units was also important in maintaining the continuity of the data. For this reason, PVC push rods with position markers were used to position the sondes within the same location of the holding pipes even though blocking bolts were placed in the ends of each pipe. Each push rod was taped to the sonde and cable, and a mark indicating position was placed on the end of the push rod. This allowed the depth of the sonde to be consistent throughout the comparison. If differences in depth were allowed between data sets, changes in the dissolved oxygen, specific conductance, temperature, and pH would be expected.

Each of the sondes had a probe cluster shield or protective shroud around the probes. Both shrouds had openings that would allow sufficient water flow across the probes even at the lowest flow rates. However, the larger the openings, the higher the chance of damage would occur to the probes due to drifting debris. This occurred, and the YSI was damaged. Debris punctured the DO membrane, and data was lost for one deployment period. In order to reduce the chance of further damage, YSI recommended wrapping the shroud with nylon screening, and adjusting the size of the screen apertures to increase water flow needed to achieve adequate water flow. The YSI used in this study was wrapped, and pre and post wrap measurements were made to ensure that no differences in measurements were observed. Another problem was encountered with the shrouds or calibration cups. Once even slightly snug, the calibration cup on the YSI sonde was most difficult to remove, and sometime required two people to loosen the cup. There was no such difficulty with the Hydrolab sonde.

COMPARISON OF WATER-QUALITY PARAMETERS

While no statistical analysis was done to examine the collected parameters, time-line graphs were sufficient to note similarities and contrast the abilities of the two compared sondes. Measurements of temperature and specific conductivity were identical or very similar for all of the deployment periods, and time-line graphs exhibited no differences in measurement capabilities between the two sondes for these two parameters. However, pH, dissolved oxygen, and turbidity all had noticeable differences in their measurements for most deployment periods.

Hydrogen-Ion activity (pH) is basically a measurement of the concentration of H^+ that is expressed in a logarithmic unit, and the abbreviation of pH represents the negative base-10 log of the hydrogen ion (Hem, 1992). Both sondes use technologies that measure the gradient in the hydrogen ion concentrations between the inside and outside of the probe's sphere as millivolts. The gradient measurements are a near constant relationship, and the measurement technique uses an equation to relate a pH unit from the millivolt measurement. Since the pH data sequence and periodicity were similar for both of the sondes during most deployments, and calibrations were consistently valid, and no trouble-shooting prompts were produced during calibrations; pH measurements appear to be within the operating specifications for both of the sondes. However, there was a consistent difference in the pH reading of approximately 0.4 pH unit (Graph 1). Due to the similarity in data fluctuation through time, the measurement offset must have been based in the probe's millivolt to pH unit equation, and the difference in the reading was probably a result of slightly different equations used in the software.

Concentrations of dissolved oxygen (DO) in surface waters is a function of water temperature and barometer pressure, and to a lesser extent, the concentration of other solutes (Hem, 1992). In lotic systems experiencing light to moderate eutrophic conditions, such as Bear Creek, the balance of ambient DO concentrations is maintained by the hydraulic mixing properties of the stream and the photosynthetic production of oxygen by algae and aquatic plants. This production is offset by the consumption of DO

by the decomposition of organic matter and respiration of aquatic plants and animals. It is the surplus DO that is measurable, and the magnitude of the diel periodicity can indicate various levels of eutrophication during the warmer portions of the year.

Deposition of organic matter in and around the probes of a sonde can change the redox potential of the water and thus interfere with the interpretation of the measurements. Although water flow was maintained in the holding pipes during the study, organic debris buildup would collect in the end of the sonde shield creating a sediment and biofouling situation. The fouling of DO probes was expected to be the most frequent cause of DO data drift as indicated by the USGS staff, but during this study, data drift was not considered as high as that observed in other enriched systems. Sonde DO comparison suggested that although the Hydrolab tended to drift more through an average deployment period, variability of the data through time was less in magnitude than the YSI (Graph 2). The time-line graph is typical of DO collections for the winter months. Both sondes document the periodicity of the parameter, and early in the deployment the YSI exhibited little data fluctuation between readings. However, during the later portion of the deployment the YSI began to show increased fluctuations between readings and the time-line graph begins to take on a fuzzy appearance. Notice that on the turbidity graph (Graph 3) that there was a flood event, and the turbidity readings were over 1000 NTU. After that flood event, the YSI DO collections began to show a higher frequency of between-sample variation. The increased fluctuations are interpreted to be a product of fine sediments deposited within the shroud by the flood event, and may point out a weakness in the YSI's approach to measuring DO. The YSI Rapid Pulse™ system does not use a stirring device in order to measure dissolved oxygen thus in order to ensure a proper volume exchange within the probe shroud, the sonde must be placed in flowing water. Since the shroud was wrapped with nylon screening to protect the probes from drift damage, the fine sediments produced by the flood event must have been clogging the shroud portals to the extent that water volume exchange was compromised and sedimentation was effecting the measurements. Since the probe would calibrate and all fluids within the probe were of ample quantity, the clogging scenario would sufficiently explain the variation that was produced in the data that was collected by the YSI. In order to preclude this situation while monitoring streams such as Bear Creek, the screen should not be used and post-flood site visits should be made to in order to ensure that the DO membrane was not damaged by the flood.

The performance of the turbidity sensors was similar. Both sondes featured a sensor outfitted with an optical wiper, and performance throughout the range in turbidity was similar. However, Hydrolab's probe would only measure to 1000 NTU (Graph 3), and several of the storm events were greater than 1000 NTU in magnitude. This may be problematic, depending upon the needs of the project. Measurements at these concentrations are challenging at best under laboratory conditions, and an *in situ* measurement at this concentration is only a good estimate at best. Further comments on the capabilities of the turbidity measurements may be redundant due to the up grades in probes that both companies have recently made, see above websites.

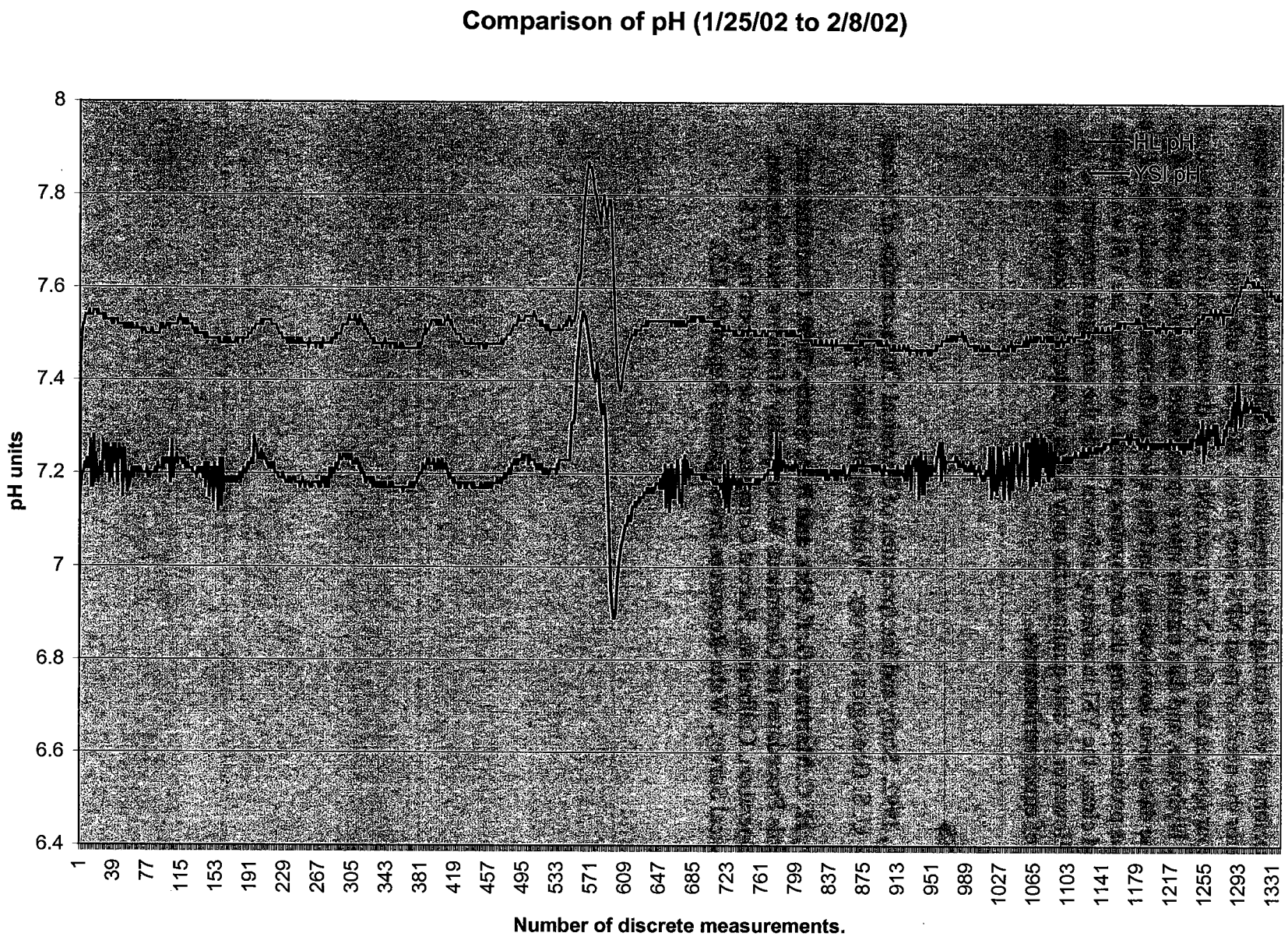
OVERALL RECOMMENDATIONS

Both sondes performed well during this comparison, and either product would be more than adequate for the needs of most NPS study units. However, after using both products, it is our opinion that the YSI is preferable. YSI downloaded data in a third of the time of the Hydrolab, and data transfer into a spreadsheet format was simpler. Also, YSI graphed the data upon downloading, and this allowed the user to visually check the data for obvious problems during the deployment period. Although the YSI was harder to calibrate and clean, the YSI interfacing software made the strongest argument as to preferability. However, if data quality is the only factor in selecting a sonde, then both products were of equal performance.

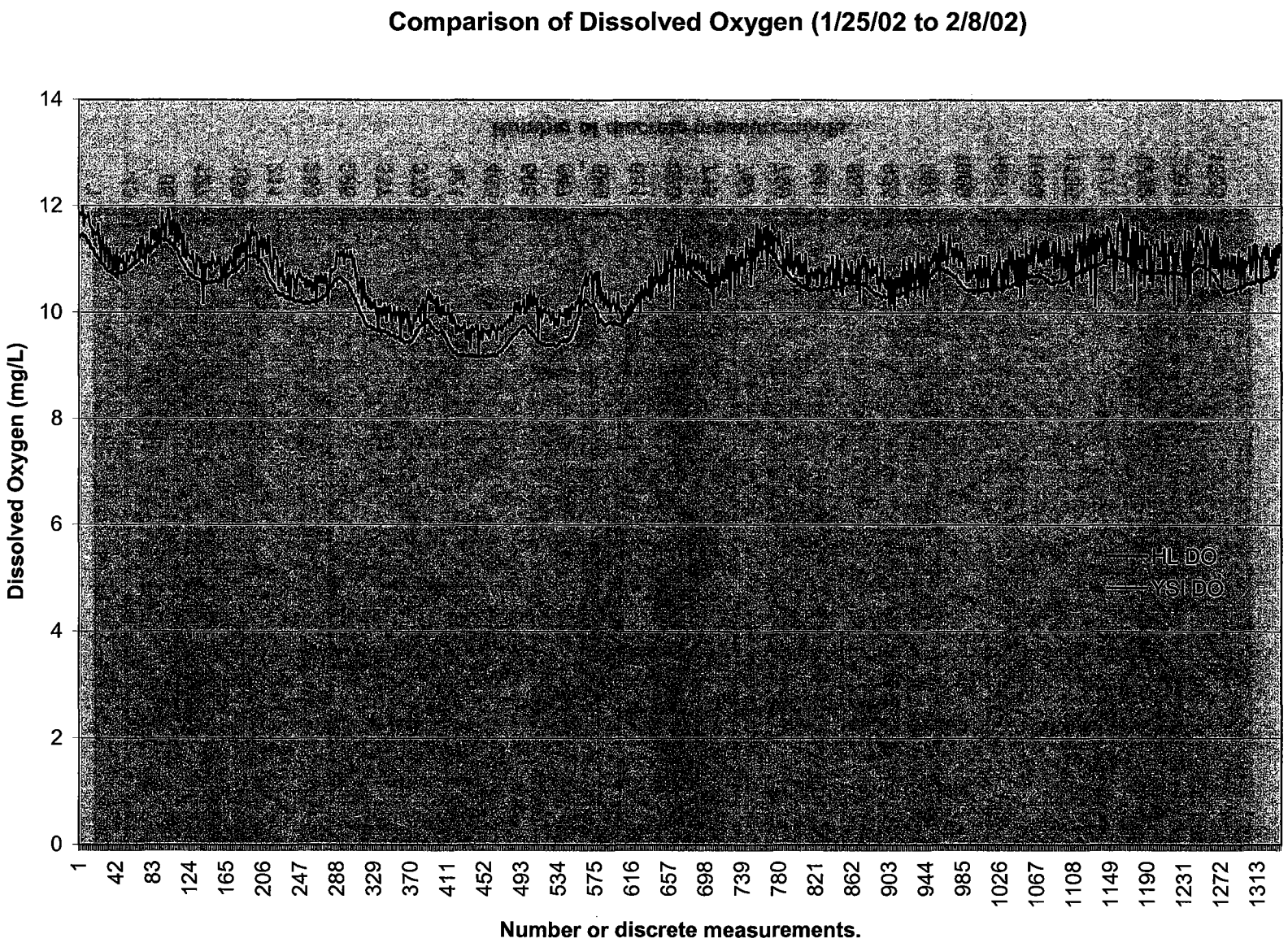
REFERENCES

Hem, John D., 1992. Study and Interpretation of Chemical Characteristics of Natural Water. U. S. Geological Survey. Water-Supply Paper 2254.

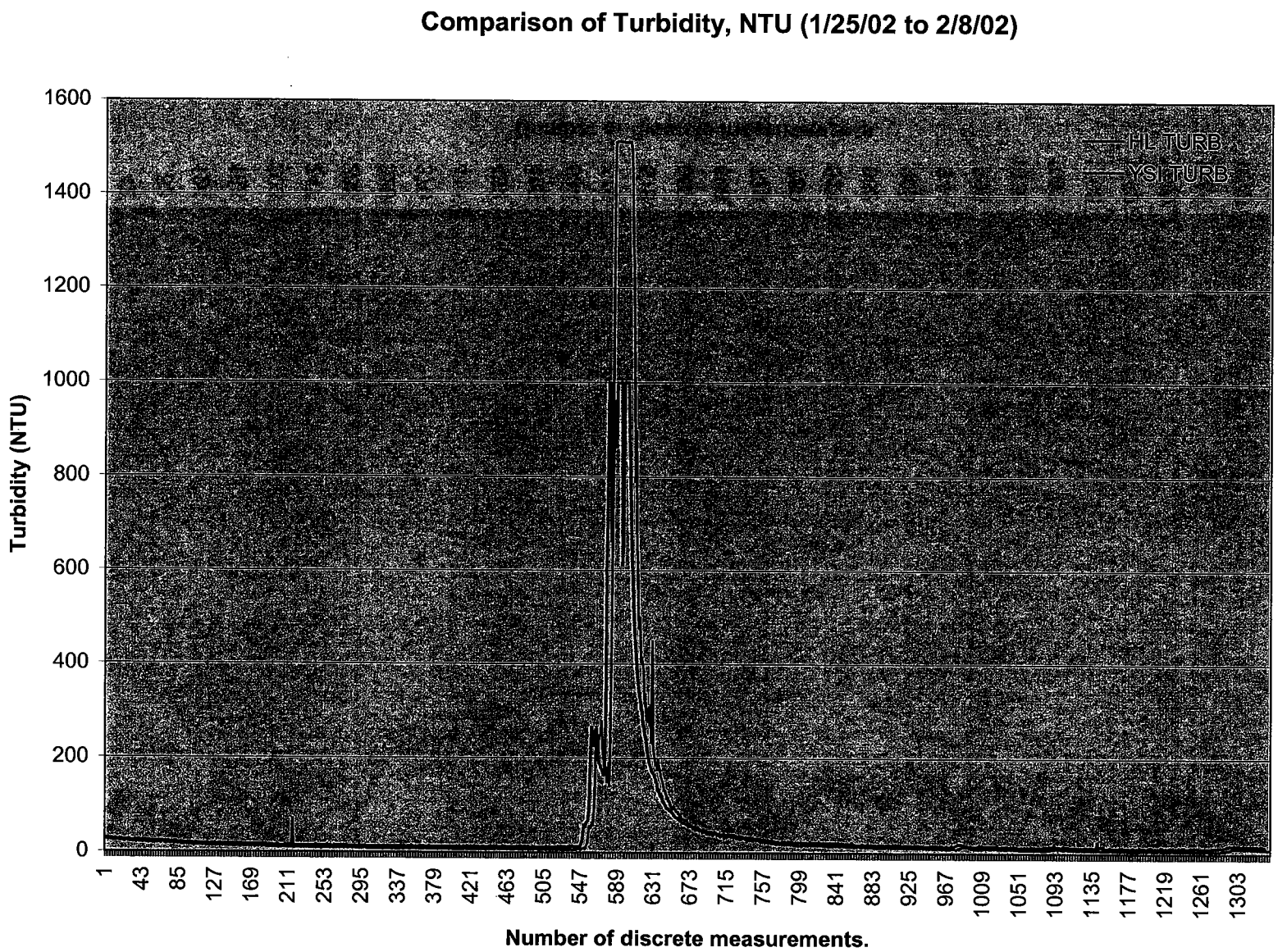
Wagner, R. J., H. C. Mattraw, G. F. Ritz, and B. A. Smith, 2000. Guidelines and Standards Procedures for Continuous Water-quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting. U. S. Geological Survey, Water-Resources Investigations Report 00-4252



Graph 1. A sample of the difference in pH during the period of January 25th to February 8th, 2002. YSI pH data is graphed on the upper line. Notice sequence and periodicity is similar but readings differ approximately by one pH unit. Both meters were functional and in calibration.



Graph 2. A sample of the difference in dissolved oxygen (DO) during the period of January 25th to February 8th, 2002. YSI DO data is graphed on the upper line and exhibits more between-sample variation.



Graph 3. A sample of the difference in turbidity during the period of January 25th to February 8th, 2002. The Hydrolab was limited to readings below 1000 NTU.