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Let's Solve Water

Case study
YSI • XA00358

Continuous monitoring of water utilities in the UK using the EXO Ammonium ISE

The Environment Act 2021

In 2021, the United Kingdom passed the Environment Act (EA 21), a pivotal legislative framework for environmental protection. Section 82 of EA 21 establishes stringent regulations for water quality to safeguard aquatic ecosystems and ensure the health and safety of the population. This section delineates the criteria and standards that must be met to maintain or enhance the quality of waterbodies across England. It calls for regulatory agencies to actively manage and monitor water pollution sources, requiring that all discharges, whether industrial, agricultural, or municipal, adhere to prescribed limits on contaminants.[1]

Among the water quality parameters of concern in Section 82 are temperature, dissolved oxygen, pH, turbidity, and ammonia. Maintaining compliance requires water companies in England to continuously monitor water quality upstream and downstream of all combined sewer overflows (CSOs) and sewage treatment works that discharge into a watercourse, which is especially important during heavy rain events when sewer pipe capacities are exceeded, causing untreated sewage to spill into the environment.[2]

Application
Effluent & stormwater monitoring

Client
Wastewater management

Xylem's role
Deployment and data collection

Project results
Real-time ammonium data from EXO sensors viewed on HydroSphere can provide valuable insight on sewage overflow events for Environment Act monitoring in the UK.

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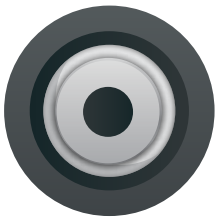
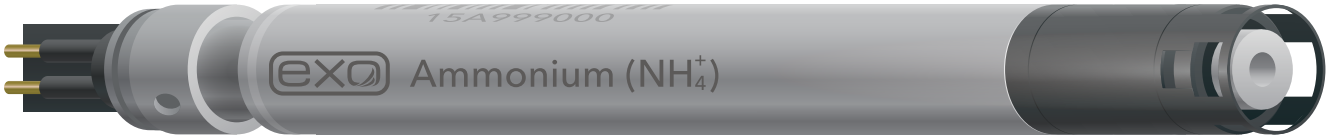
Ammonium ISEs for freshwater monitoring



Ammonium and ammonia are important to monitor because they can indicate industrial, agricultural, and wastewater runoff, and high concentrations can enhance the growth of algae and macrophytes and are potentially toxic to aquatic organisms. Ammonium Ion Selective Electrodes (ISEs), such as those compatible with the YSI EXO Multiparameter Sonde, can measure ammonium directly in the water column using proven electrochemical techniques that specifically measure ammonium (NH_4^+) ions.



The EXO Ammonium ISE uses a silver/silver chloride wire electrode in a custom reference solution to measure the potential across a membrane that depends on the relative concentration of ammonium ions in the water. The sensor is ideal for freshwater (<1500 µS/cm) because ionic species in saltwater can interfere with the measurements. Ammonia is a calculated parameter and is dependent on temperature, salinity, and pH. The sensor references live measurements from the EXO Conductivity/Temperature and pH sensor for the most accurate ammonia data. This makes the Ammonium ISE a valuable tool for monitoring ammonium and ammonia in freshwater environments, especially those impacted by CSOs.

Historically, Ammonium ISEs have been used for discrete measurements rather than deployments since they could be prone to drift and require frequent calibration. Combined with their accuracy specification of ±2 mg/L-N, this created a limitation for the use of the sensors to achieve the continuous monitoring required of water utilities by EA 21. Improvements to sensor technology and calibration techniques have enabled Xylem to use these sensors for monitoring applications.

To make the case for the use of the EXO Ammonium ISE in long-term deployments to provide data on the impact of sewage overflows and wastewater effluent during storm events in real-time, Xylem UK worked with the Environment Agency and several English water companies to install EXO2^S sondes with telemetry upstream and downstream of wastewater final effluent and sewage pumping stations.

Long-term deployment testing

Beginning in 2022, two EXO2[S] sondes were installed in the receiving water upstream and downstream of a sewage pumping station to monitor water quality and the impact of the overflow tank during storm events. These site locations were chosen to bracket the effects of the effluent on the waterbody, as demonstrated by the example scenario depicted in **Figure 1**.

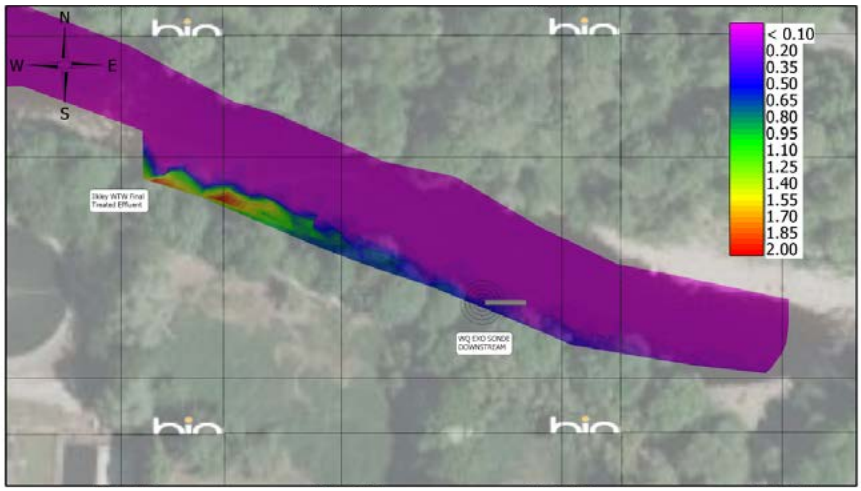


Figure 1. An example showing how the wastewater outfall location is evident from the distribution of spatial ammonium concentration data collected during a one-time survey performed with an rQPOD Remote Surface Water Vehicle equipped with an EXO Sonde.

The sondes were equipped with EXO Conductivity/Temperature, Optical Dissolved Oxygen, pH, Turbidity, and Ammonium Smart Sensors with a Central Wiper for anti-fouling. The systems were connected via cellular telemetry to HydroSphere, a cloud-based data collection platform, to view site data remotely in real-time.

The Xylem UK HydroDaaS (Data as a Service) team performed regular calibration of the sondes in a laboratory approximately every two months and swapped the sensors in the field, deploying newly calibrated sensors and retrieving field sensors due for calibration. Post-deployment checks were performed in calibration standards to determine sensor drift. Grab samples from the upstream and downstream deployment sites were collected by the water utility every two weeks and analyzed by a certified lab. The lab-analyzed data was used to compare against the data collected by the EXO sensors to check for the accuracy of the field measurements.

A site-specific correction of the sensor data using correlations to grab sample data may have improved the sensor accuracy, but the purpose of the test was to deploy sensors calibrated in a lab with standard solutions to represent the most user-friendly and direct approach to collecting field measurements.

Upstream

Downstream

EXO sensor stability and accuracy

All sensors demonstrated high stability during the deployments. Post-deployment checks showed minimal sensor drift. Most EXO sensors, including Optical DO, Turbidity, and Conductivity/Temperature experience very little measurement drift over time; after calibration and subsequent deployment, they read very close to the calibration value in standard after removal from the field. Historically, ISE sensors tend to drift more readily during deployments; however, the EXO Ammonium ISE sensor drifted only 0.25 mg/L at the upstream site and 0.31 mg/L at the downstream site over a 73-day trial period. The reliable stability of the sensors allowed the team to adhere to a 2-month cycle of swapping deployed sensors with calibrated sensors.

The EXO sensor measurements were highly accurate when compared to the lab-analyzed grab samples. For example, the Turbidity and pH graphs (**Figures 2 and 3**) demonstrate the tight correlation between the lab and field data. The data also demonstrate the benefit of the granular, event-based data that field sensors can provide over grab samples.

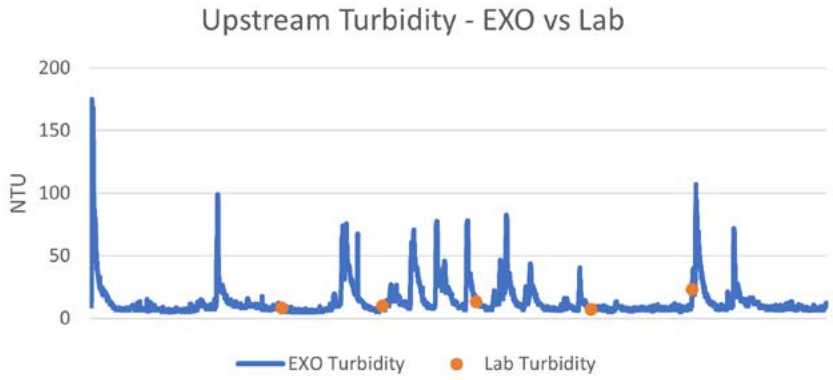


Figure 2. Upstream site EXO Turbidity sensor data with lab-analyzed grab sample data.

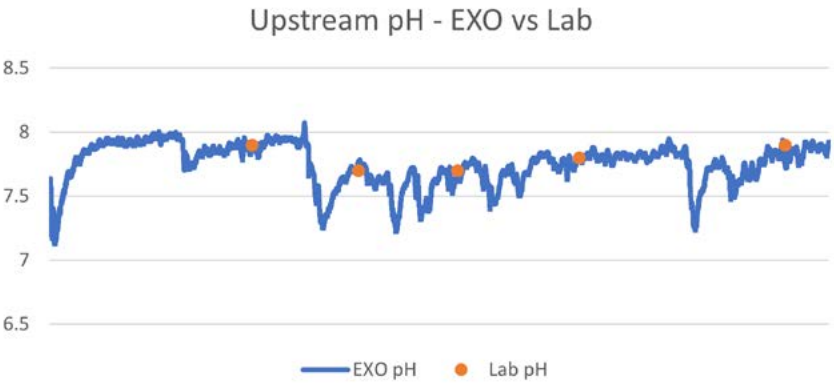
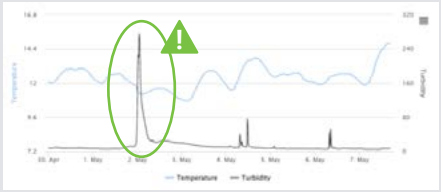


Figure 3. Upstream site EXO pH sensor data with lab-analyzed grab sample data.

HydroSphere for real-time data

The ability to view real-time data in HydroSphere allowed the team to monitor the site conditions as storm events occurred.

They not only watched for spikes and changing indicators in the live data, but also set customizable alarms to notify them by email and text of low batteries, high turbidity events, changing temperatures, and more.



They were able to stay aware of situations that may require in-person visits; to clear out accumulated debris, fouling, and sediment, maintain the deployment structures and replace parts, swap out sondes, and collect grab samples.

Learn more about HydroSphere.

The Ammonium ISE collects direct measurements of the ionic concentration of ammonium (NH_4^+) in the water. Ammonium measurements averaged 0.21 mg/L at the upstream site and 0.24 mg/L at the downstream site in a four-month subset; the downstream data is more right-skewed with more high-value measurements during storm events than at the upstream site (**Figure 4**).

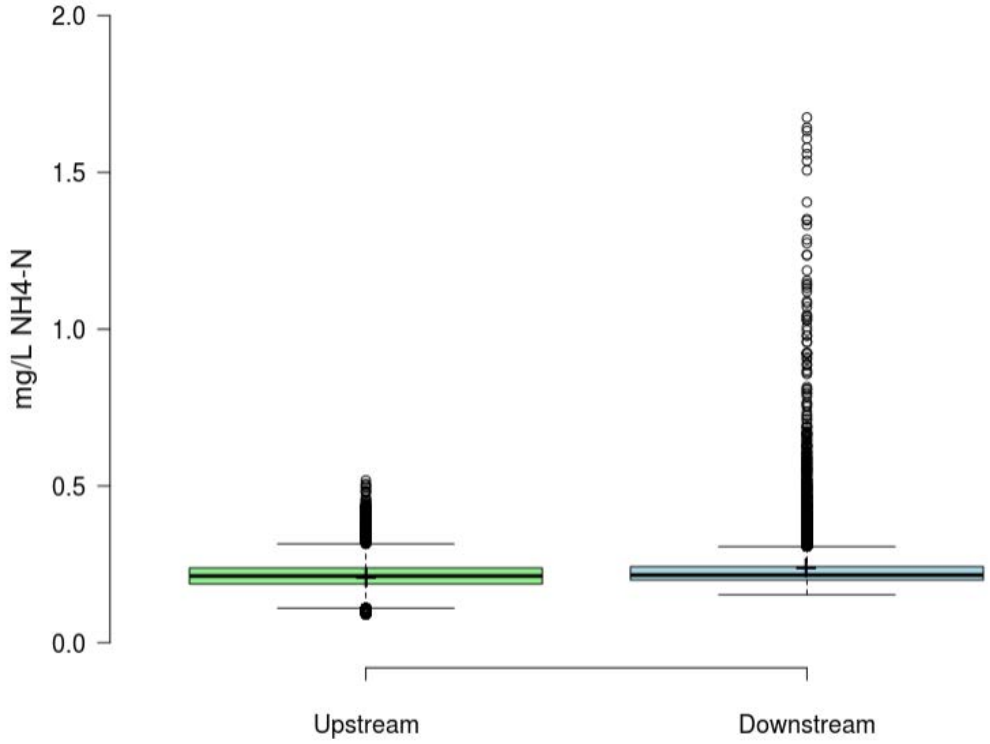


Figure 4. Boxplot distributions of the ammonium concentrations at the upstream and downstream sites.

The ammonia (NH3) measurements were consistently close to zero (about 0.001 mg/L) due to the effect of pH, which was between 7 and 8, on ammonia solubility.[3] Ammonia therefore had a minimal contribution to the summation of ammonia and ammonium measurements when comparing against laboratory results in Total Ammonia Nitrogen (TAN). Interfering species, such as halide ions, can cause false positive ammonium measurements of up to 0.5 mg/L higher than lab results. However, throughout the deployment test, the Ammonium ISE only read approximately 0.2 mg/L ($NH_4^+ + NH_3$) higher than the laboratory results (TAN), exhibiting high accuracy compared to grab samples (**Figure 5**).

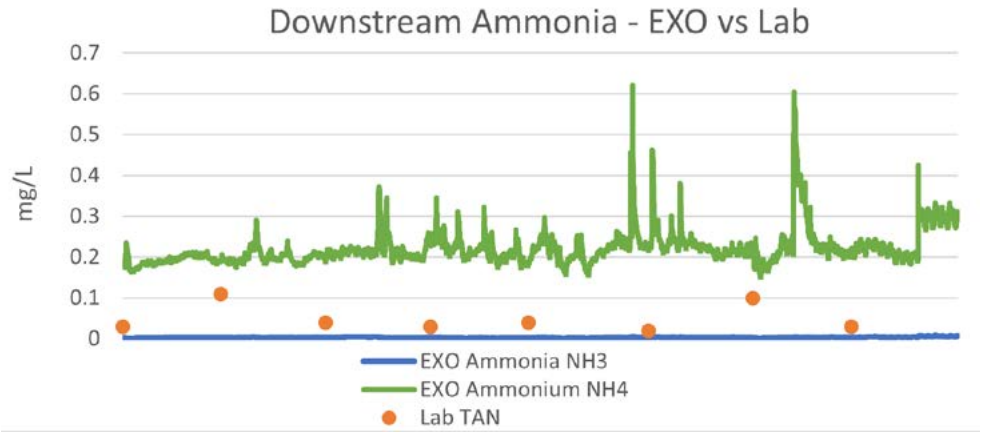


Figure 5. EXO ammonium and ammonia concentrations with lab-determined Total Ammonia Nitrogen (TAN) at the downstream site.

While the sensor's total measurement range is up to 200 mg/L, it excels in the low-end sensitivity, within the 0 – 10 mg/L NH4+-N range. According to local data, most UK surface waterbodies have total ammonia concentrations less than 1 mg/L, making the EXO Ammonium ISE ideal for these freshwater monitoring environments.

Monitoring sewage overflows

From the live data in HydroSphere, rainfall events were evident from decreases in pH and specific conductivity due to the effects of precipitation and dilution from increased flow. The storm events caused increases in turbidity likely from runoff and resuspension of sediment. The turbidity spikes tend to correlate with increased ammonium. During baseflow, ammonium measurements at both the upstream and downstream sites were around 0.2 mg/L. During storm events, the ammonium concentration downstream of the water treatment plant tended to be higher than upstream (**Figures 6 and 7**, orange boxes). For example, an event in April saw 0.49 mg/L of ammonium upstream, and 0.59 mg/L downstream of the sewage pumping station.

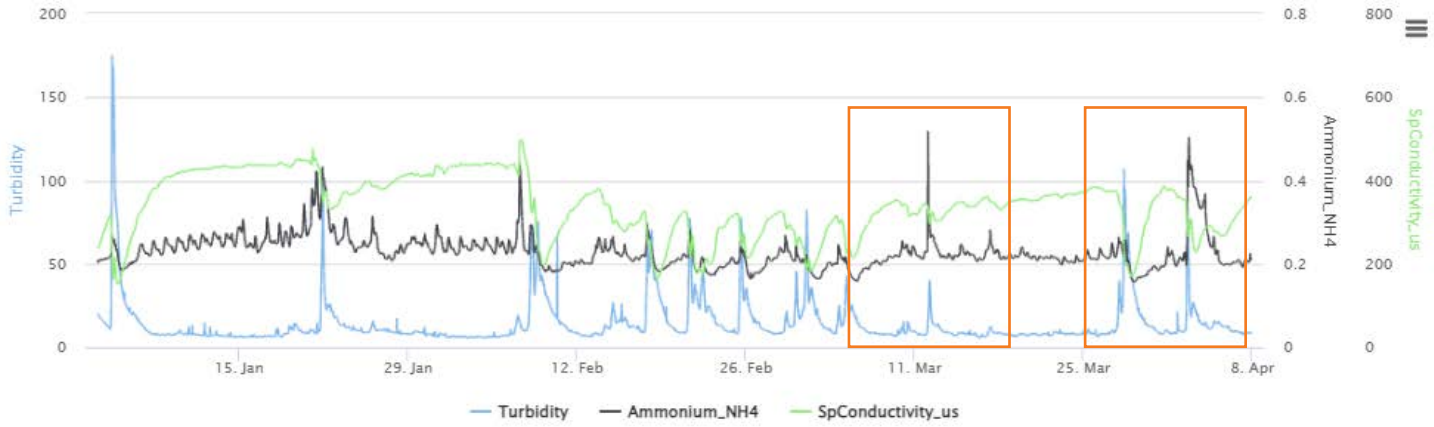


Figure 6. Upstream site EXO sensor data from HydroSphere. Rain events are correlated with low specific conductivity and spikes in turbidity and ammonium.

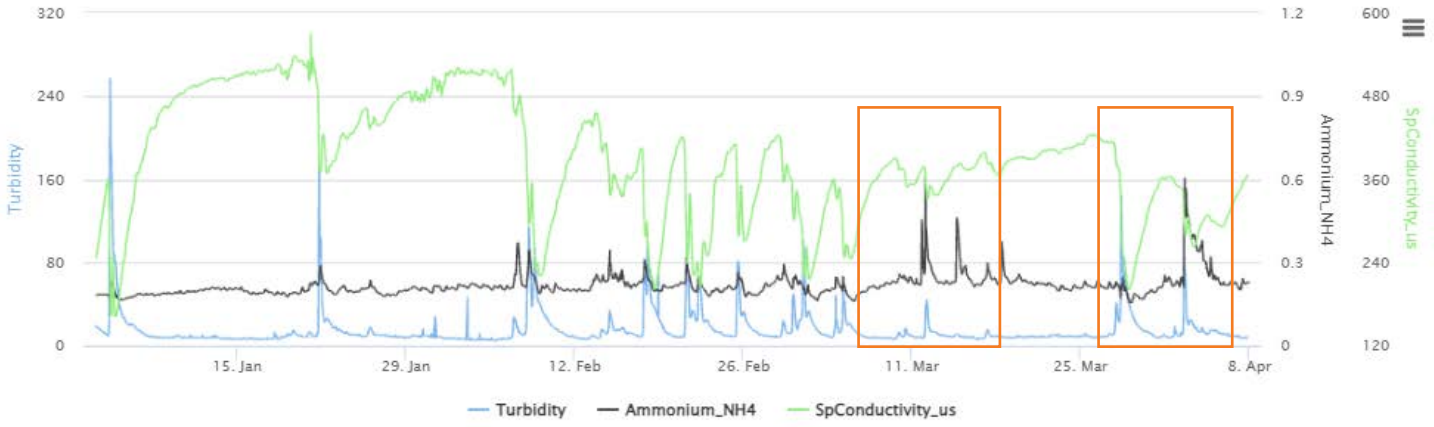


Figure 7. Downstream site EXO sensor data from HydroSphere. Rain events are correlated with low specific conductivity and spikes in turbidity and ammonium.

The sensor data can help differentiate between storm events in which sewage overflow discharges occur and those that do not. For example, in this graph of the downstream data (**Figure 8**), the pink box indicates a large increase in Turbidity, above 200 NTU, and decrease in specific conductivity that occurred during a storm event. This was followed by only a small increase in ammonium.

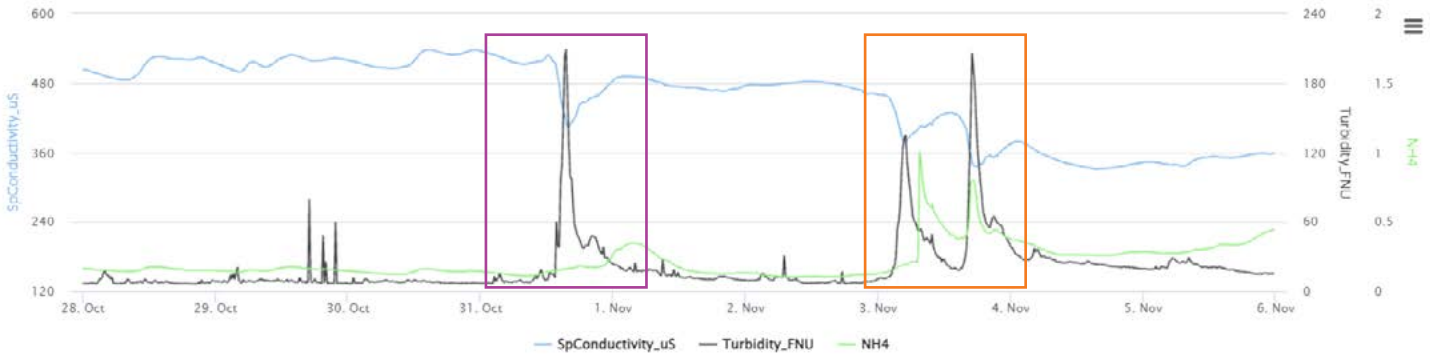


Figure 8. Downstream site live EXO sensor data excerpt from HydroSphere. Rain events during which a sewage overflow discharge demonstrated higher increases in ammonium.

However, during a later rain event outlined in the orange box (**Figure 8**), the sewage pumping station recorded an overflow event using an Event Duration Monitor, a system that reports storm-related discharges. The overflow event correlated to the increase in ammonium downstream of the sewage pumping station. Although the ammonium peaked around only 1 mg/l, this is a significant increase compared to baseflow conditions and events without recorded sewage overflows. This data set demonstrates the sensitivity of the EXO Ammonium ISE for monitoring sewage overflows in freshwater, highlighting why the Environment Agency deploys these sensors in hundreds of sites in the UK.

Other ammonium sensors

The EXO Ammonium ISE has exhibited high accuracy during the deployment studies performed by Xylem UK in partnership with the Environment Agency and local water companies, and the data show the sensor is capable of ± 0.5 mg/L NH_4^+-N from 0 – 2 mg/L NH_4^+-N. To date there is no direct measurement for ammonium with an optical sensor, making the Ammonium ISE the best choice for measuring ammonium ion concentrations in freshwater applications.

In wastewater process applications, a rugged probe able to withstand a harsh environment and frequent cleaning with a higher measurement range is ideal. The IQ SensorNet Ammolyt or VARiON sensors work well in these high ammonium wastewater applications but are less accurate at < 1 mg/L NH_4^+-N, and hence are not ideal for freshwater sites. On the other hand, for drinking water treatment applications where the measurement range needs to be even lower, from 0 to 0.3 mg/L, the Alyza Ammonium Analyzer for IQ SensorNet provides the most reliable data even at very low NH_4^+ concentrations.

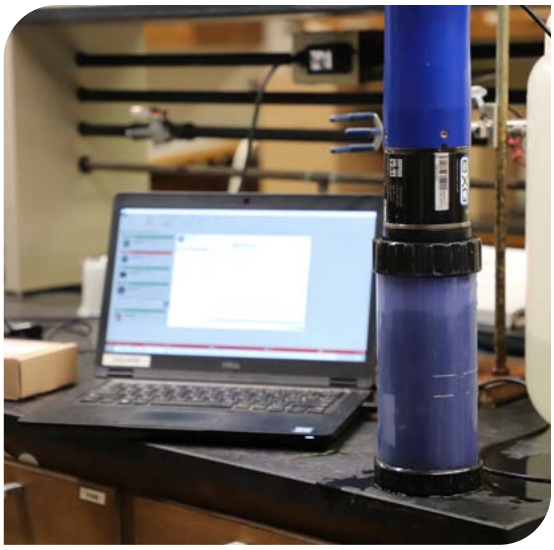
Conclusion

The deployment study is ongoing and continues to provide valuable real-time data for the water utility company. EXO field sensors, specifically the Ammonium ISE, can provide highly sensitive yet reproducible data that allows the user to respond quickly to field conditions and have high confidence in their data, especially when paired with telemetry for real-time data in HydroSphere. The data demonstrate that deployed sondes equipped with Ammonium ISEs can produce reliable long-term data in freshwater to replace or supplement grab samples analyzed by a lab for monitoring sewage overflows and compliance reporting in accordance with the Environment Act 2021.

Successful deployments with the EXO Ammonium ISE

Methods to obtain stable, accurate, reliable data with minimal drift using the Ammonium ISE for freshwater deployments.

- Perform sensor calibrations in the lab or office and swap calibrated sensors with field-deployed sensors. Lab-based calibrations allow for more controlled and reproducible conditions, such as stable temperatures and decreased contamination issues.
- Use good lab techniques during calibrations, such as using a clean sonde guard and calibration cup, removing field wiper brushes, rinsing the sonde and sensors with deionized water and drying with lint-free wipes, and triple rinses in calibration standard.
- Pre-soak the Ammonium ISE tip overnight in 100 mg/L ammonium standard, or the standard closest in value to the site, before calibrating and deploying. Soaking improves the sensor performance and increases the life of the module by removing contaminating ions and reconditioning the membrane.
- Replace the ISE module every 6 months at minimum, or as needed. The study had success with 6-month replacements, but more frequent replacements (every few weeks) may be necessary for the best data. The sensor body does not need to be replaced.
- Calibrate sensor multiples together in a batch on one sonde. Multi-sensor calibrations ensure the data are comparable between all deployed sondes and adhere to the same quality standards.
- Use the Wiper Guard for the Ammonium ISE (599864) in high-fouling deployments with a Central Wiper to protect the sensitive membrane from the bristles. Note that the guard may cause the wiper bristles to splay more quickly.
- Regularly maintain the deployment site and clean heavy fouling from the sonde and sensors.
- Perform post-calibration and post-deployment checks to measure possible sensor measurement drift against a known and traceable standard.
- Optionally, to further improve sensor accuracy, apply a site-specific offset to the data. Collect grab samples from the deployment site, measure the ammonium concentration using lab analysis or a photometer, and use the reference data to calculate an offset value to apply to the deployment data.



Calibrate sensors in the lab or office using clean equipment for more consistent results.

The EXO Central Wiper reduces fouling on the sensor faces, while the Ammonium ISE wiper guards protect the ISE membranes.

Replace the ISE module every 6 months, or as needed.

Benefits of the EXO Ammonium ISE

- Uses a direct electrochemical measurement of ammonium ions
- Up to 6-month consumable module life; sensor body can last for years
- Low cost
- Low power consumption
- High stability over deployments
- Highly accurate at low measurement range (0-2 mg/L), with full range up to 200 mg/L
- Utilizes the EXO Sonde platform with field-tested EXO Sensor features:
    - Rugged titanium build
    - Wet-mate connector
    - Smart Sensor with SmartQC
    - Powerful Anti-fouling with the Central Wiper
    - Up to 7-sensor payload
    - Automatic sensor recognition
    - Universal sensor ports
    - 3-year sonde warranty

References

1. Department for Environment Food & Rural Affairs, Continuous Water Quality Monitoring Programme
2. Environment Agency, Combined Sewer Overflows Explained
3. Environmental Protection Agency, Ammonia

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