BACKGROUND
A Gulf Coast ethylene unit with a very complex dilution steam system has created quite a challenge for their operations team. Due to tightened environmental regulations, many process streams not necessarily intended for quench water systems, have been introduced to the unit over the years. As a result the process water has become very turbid (oil in water often containing some solids), and the pH has propensity to swing, making it difficult to control. The key business drivers were to quantify how significant these swings were and the risk to the overall quench water system. The customer's main goal was to understand what was driving the process upsets and the actual conditions in their Quench Water Tower (QWT). The QWT is the heart of the dilution steam system considering all downstream equipment is impacted by its operation. It can limit production and if shutdown can often cause an unplanned outage. The customer's main concern for this tower was pH measurement, which was not readily available and had to be measured by a handheld unit once a shift. This left the QWT vulnerable to process swings that could go undetected in between measurements.

A QWT unit operating in a low pH regime could cause accelerated corrosion and fouling, unplanned shutdowns requiring import steam, or catastrophic failure, which could cause the system to remain offline indefinitely. Measuring pH manually requires operations personnel to use protective gear in order to reduce exposure to hydrocarbons, which also presents a safety concern. As a result, there is a desire to adequately detect online continuous pH measurement and control using a new technology and limit their personnel to potential safety exposure.

SOLUTION
After discussing the initial concerns with the customer, a full system survey and Best Practice Gap Analysis (BPGA) Audit were utilized to quantify the risk. The BPGA identified the following action steps:
• Track and analyse samples of the quench water free iron data and O₂
• Quantify recycle stream quality
• Further investigate the presence of unknown acidic species uncovered by the BPGA
• Utilize the real-time 3D TRASAR for Dilution Steam Systems (3DT-DSS) data to try and correlate the plants unplanned events to upstream process issues

After reviewing the results with the customer, Nalco Water recommended using the new 3D TRASAR for Dilution Steam Systems (3DT-DSS) technology to provide a continuous solution rather than only providing a “snapshot” per the BPGA. Initially the customer measured the pH using a standard handheld device to compare against the 3D TRASAR system to confirm the 3DT-DSS results. A six-week evaluation period was chosen. The trial process was as follows:
• Establish a clear process baseline:
  - Increase standard sample frequency by using a handheld pH - measurements twice a shift vs once a shift
• The 3DT-DSS configuration:
  - Sample point: QWT bottoms recycle
  - pH measurement: every ten minutes using dual pH probes to ensure accuracy
  - Online turbidity measurement using proprietary Nalco Water fluorometer
• Trial expectations/Success Criteria:
  - Demonstrate the 3DT-DSS could reliably measure pH against a manual measuring
  - The accuracy with handheld pH measurements within +/- 0.5 pH units 90% of the time

VALUE DELIVERED
Reduced hazardous exposure man hours
700 hrs/yr
RESULTS
After calibrating the handheld and surveying twice a shift for six weeks, the results were plotted against the 3DT-DSS pH, shown in figure 1. The 3D TRASAR unit was not only very accurate against the handheld, it delivered results greater than 90% success criteria. Further analysis was performed to understand what data the online measurement captured that the manual method might have missed (Figure 2). Looking at the full online 3DT-DSS results, there were multiple periods where the pH dipped in between measurements which would have gone unnoticed had it not been for the 3D TRASAR unit. Figure 3 not only highlights these missed pH excursions, but also identified bias error in the handheld itself. This bias was discovered by the 3DT-DSS system because of the units redundant probes. Only after seeing both TRASAR pH readings consistently tracking similar values and the handheld readings diverging from the TRASAR’s output(s), was the hand-held recalibrated.

These pH excursions expose the unit to potential emulsions, foaming, corrosion, and accelerated fouling. After reviewing with operations personnel, it was identified that the error in the hand-held was due to contamination in the probe. Again, this would not have been captured without the dual pH probes to validate the problem and launch an investigation into the error.

CONCLUSION
In summary, the trial results are as follows:

<table>
<thead>
<tr>
<th>Trial Criteria</th>
<th>Delivered</th>
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<tbody>
<tr>
<td>+/- 0.5 pH</td>
<td>+/- 0.3 pH (all data points)</td>
</tr>
<tr>
<td>90% of the time</td>
<td>91% (all data points)</td>
</tr>
<tr>
<td>Time within +/- 0.5 pH</td>
<td>100%</td>
</tr>
<tr>
<td>Percent Error</td>
<td>2%</td>
</tr>
<tr>
<td>pH Deviation</td>
<td>+/- 0.1 pH</td>
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Moving forward the customer decided to keep the unit online and has begun implementation of pH control to prevent these pH swings from occurring in the future. The trial also identified a process control issue with an upstream waste gas unit that was liberating excess acid into the quench system. This has since been resolved.