

# Evaluation Project Results



Ammonia Removal Processing Line

## 3.1 Ammonia Reduction

EvTEC performed sampling at various times throughout the pilot plant operations. Of the approximately 25,200 gallons (95,382 liters) treated during the 3-month pilot demonstration, EvTEC was able to obtain composite samples representing approximately 9,500 gallons (35,956 liters), or about 38%, of the total treated flow. Table 3-1 provides a summary of relevant statistics for the ammonia samples collected and analyzed by the EvTEC contract laboratory during the evaluation testing. Approximately 89% of the ammonia influent to the adsorption columns was removed. Appendix A of this report provides the laboratory analytical data from ACCUTEST<sup>®</sup> and Appendix B provides a summary of the flow and laboratory data in tabular form. FWENC calculated a mass balance closure of 97% for ammonia around the columns. More detailed information on this closure information can be obtained from ThermoEnergy and FWENC.

Statistic	Influent Concentration (mg/L NH <sub>3</sub> -N)	Effluent Concentration (mg/L NH <sub>3</sub> -N)	Percent Removal (%)*
Mean (Flow Weighted)	280	31	89
Maximum Influent Ammonia Value	500	116	-
Minimum Influent Ammonia Value	109	24	-

**Table 3-1. Project Ammonia Concentrations**  
\* Percentage removal based on concentrations.

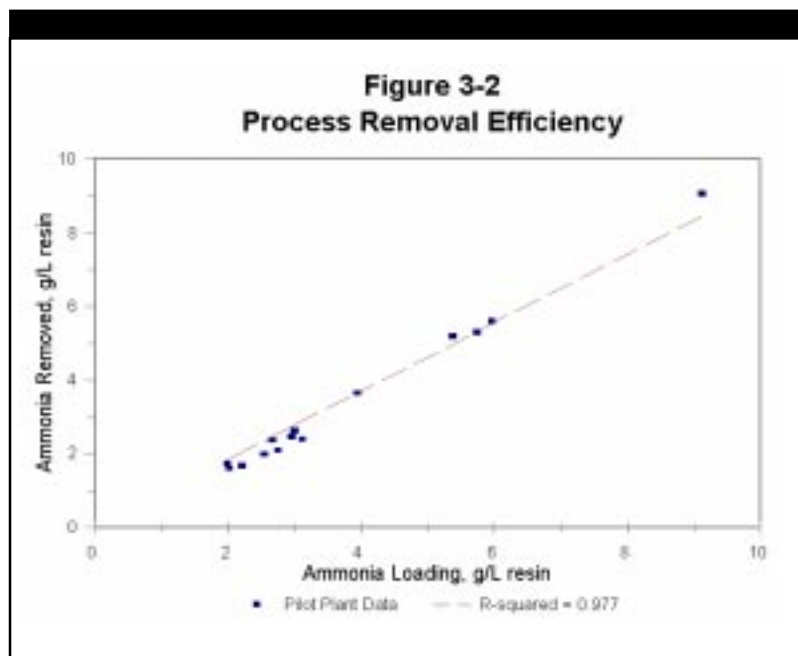
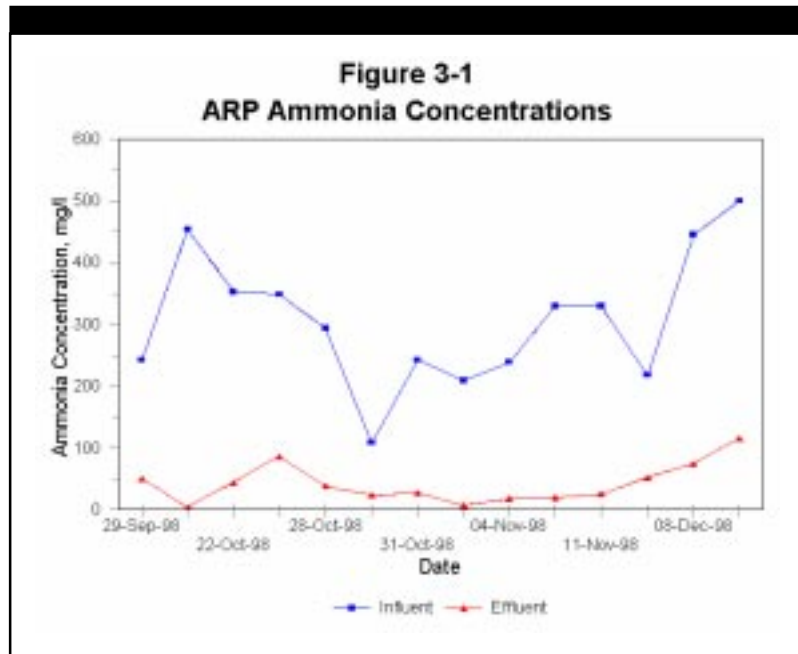
Figure 3-1 illustrates the variability of the influent and effluent concentrations experienced during pilot plant operations. Although influent concentrations were highly variable, only once during the pilot study, on December 9, 1998, did ACCUTEST<sup>®</sup> record an influent ammonia value as high as 500 mg/L NH<sub>3</sub>-N.

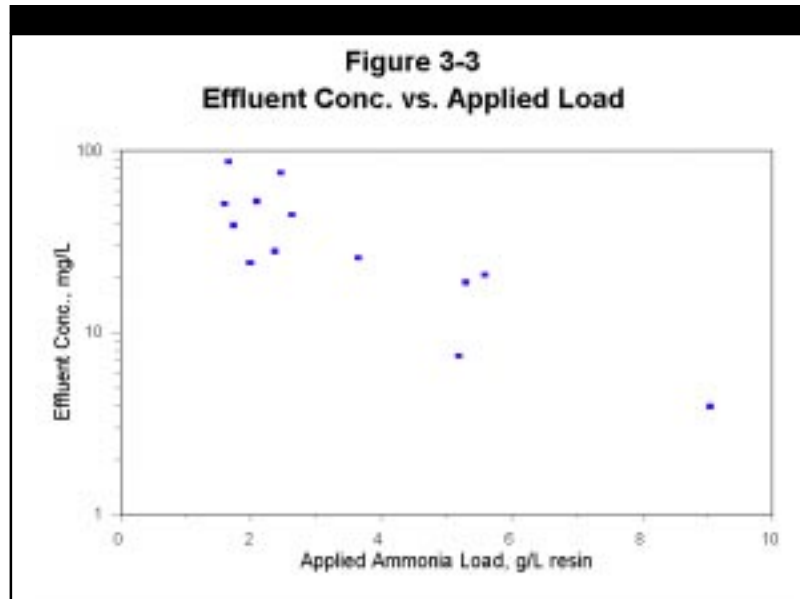
In environmental engineering, it is often desirable to relate system performance to easily measured and controlled operating variables. Quite often, loading rates are found to provide useful relationships. Figure 3-2 demonstrates ARP process performance for ammonia removal as a function of influent ammonia loading. In Figure 3-2, both flow and concentration variations are taken into account by using total mass ammonia loading per volume of resin. From Figure 3-2, it can be seen that on a mass basis, at

influent mass loadings between 2 and 9 grams  $\text{NH}_3\text{-N}$ /liter of resin. The coefficient of correlation for the relationship is 0.977.

As illustrated in Figure 3-3, the data indicates that the adsorbers performed better at higher influent mass loadings than at lower influent mass loadings.

As mass loadings exceeded approximately 3 grams  $\text{NH}_3\text{-N}$ /liter of resin, ammonia effluent concentrations decreased greatly. However, while the point regarding the influent loadings has been made, it can not be stated for certain which of the two factors accounting for influent mass (concentration and flowrate) are responsible for the phenomena. In addition, it was not possible to correlate the effluent concentrations with





either the length of time for the resin column to exhibit breakthrough or the previous mass loading history experienced by either sorption column.

### 3.2 Impact of Solids on the ARP Resin

Shortly after initiating centrate processing through the ARP, it became apparent that influent solids were resulting in detrimental operations at the 75 and 10 micron bag filters used for pre-treating the influent waste stream. To reduce the number of times needed to backflush and/or change the filters, FWENC added a 500-gallon cone-settling tank upstream of the bag filters to assist in removing a large percentage of the ARP influent solids. Solids removed from the settling tank were returned to the Oakwood WPCP plant sewer. Based on 16 grab samples collected by the EvTEC contract laboratory, the influent solids concentration to the

settling tank averaged approximately 760 mg/L TSS and samples from the bag filter effluent dropped to 60 mg/L TSS. Solids concentrations in the ARP effluent typically were below 10 mg/L. Therefore, while no definitive upper bound on suspended solids influent to the ARP which will not result in a problem can be inferred, based on the available data it appears that influent solids concentrations up to 60 mg/L have no detrimental impact on the ARP performance. Based on the experience gained during EvTEC evaluation, FWENC has recommended adding a settling tank prior to the sorption columns under full-scale operations.

### 3.3 Impact of Iron on the ARP Resin

Ferric chloride-iron is present in the centrate at Oakwood due to its upstream application in controlling struvite formation in the lines following the centrifuges. Table 3-2 provides

Statistic	Iron (mg/L)		Zinc (mg/L)	
	Influent	Effluent	Influent	Effluent
Mean (Flow Weighted)	5.19	0.80	1.12	13.50
Maximum Iron Influent Value	7.94	1.28	--	--
Minimum Iron Influent Value	3.96	1.0	--	--
Maximum Zinc Effluent Value	--	--	3.16	141.0
Minimum Zinc Effluent Value	--	--	0.16	3.70

**Table 3-2. Iron and Zinc Concentrations in Centrate and Column Effluent for sampling dates after 10/28/98**

summary statistics for the iron and zinc samples collected and analyzed by the EvTEC contract laboratory, ACCUTEST® during the evaluation.

Based on the data presented above, iron is likely exchanged with the  $Zn^{2+}$  sites in the ARP resin. The zinc loaded resin sites are also believed to be exchanged with other cationic ions and compounds having a higher affinity than zinc for ARP resin. While the independent data collected by the EvTEC contract laboratory are presented here, all three laboratories collecting samples during the project obtained similar results for iron and zinc. To compare both iron influent with zinc effluent values, Table 3-2 does not include data for the days that known ferric chloride overdosing and polymer poisoning events occurred. Table 3-2 includes data only from dates after October 28, 1998 and the reasons for this are discussed below. For iron and zinc, the EvTEC data represents approximately 5,500 gallons (20,818 liters) of the 25,200 gallons (95,382 liters) processed during the evaluation.

During the month of October, the initial break-in stage of the ARP system, ferric chloride was inadvertently overdosed at the Oakwood WPCP with a subsequent immediate reduction in  $NH_3$ -N removal efficiency in the ARP resin. This drop in efficiency was due to zinc stripping off of the resin column, and thus the ammonia had no zinc sites on which to adsorb. Although this was not seen in the zinc effluent composite sample on October 28, 1998, it is likely that the zinc stripping was immediate, and not spread over the course of the day, i.e., not captured and represented in a significant aliquot of the effluent composite sample. The physical color of the resin changed from the original tan to a reddish tint, as might be expected. Following the October 28, 1998 event, Column 1, which was in operation the previous day, was successfully regenerated using the concentrated zinc sulfate/sulfuric acid regeneration solution.

As the data in Table 3-2 indicates, the zinc effluent concentrations are much higher than influent concentrations to the ARP resin columns. As is the case with the entire iron composite sample data (from September to December), which included the ferric chloride overdose, the zinc data were somewhat skewed because of several days where zinc was significantly stripped from the resin column. The most notable examples of this occurred on October 14 (this date not included in Table 3-2) and December 9, 1998, when zinc concentrations reached 468 mg/L for 962 gallons (3,641

liters), and 141 mg/L for 299 gallons (1,136 liters) of process centrate flow, respectively. The high concentration of iron in the influent is believed to be the reason for the first occurrence on October 14, 1998, and the ARP system shut down operations taking place at Oakwood for the December 9, 1998 value of 141 mg/L for the ARP zinc effluent. The December date accounts for over half of the flow-weighted value listed in Table 3-2's 13.5mg/L's average. As mentioned above, and for comparison purposes with iron data the values listed in Table 3-2, the zinc averages, minimum and maximum effluent values listed are for sampling dates after October 28, 1998, and do not include October 14, 1998.

In summary, excessive influent iron poisoning events can result in system upset, although ARP influent concentrations anticipated to be routinely encountered in the centrate are not expected to have a long-term detrimental impact on system performance. The pilot study demonstrated that the resin could return to high ammonia removal efficiencies after such events by regenerating the resin using a concentrated zinc sulfate/sulfuric acid solution described in Section 2.2.

### **3.4 Impact of Polymer on the ARP Resin**

The polymer used to increase the efficiency of sludge dewatering operations was found to have little or no impact on the ARP resin when the dosage was regularly maintained. However, during the sampling period from October 3-7, 1998, the polymer addition process was mistakenly left in a continuous feed mode, and the ARP resin was coated with polymer. Because this occurred over a weekend and the pilot plant did not operate from October 3-6, ammonia breakthrough was experienced after processing only 60 gallons of centrate on October 6, 1998. Following breakthrough detection, the system was taken off-line and FWENC elected to replace Column 2 with new virgin resin to ensure at least one operating column for the remainder of the ARP demonstration. Column 1 was then successfully regenerated by soaking the resin with a concentrated sulfuric acid solution for eight (8) hours and then rinsing it with clean water. The entire system was then returned to processing centrate. It is important to note that this polymer poisoning event predates the ferric chloride overdose described in Section 3.3. In summary, while polymer poisoning events are likely to result in system upset and/or premature breakthrough, the resin was found to recover from the event, following regen-

eration. No discernible loss of resin ammonia removal efficiency could be concluded from the data, while sorptive capacity losses were investigated later in the evaluation and are discussed in Section 3.5.

## 3.5 Short-Term/Long-Term Resin Removal Capacity

A key issue raised by the EvTEC Panel was the long-term effectiveness (where possible) of the resin and the impact of regeneration cycles on the resin performance.

To address this issue, a series of side-by-side laboratory bench-scale comparisons of virgin resin and the resin used in the 3-month pilot plant were performed to assess, to the extent practical, the impacts of the waste stream (including any contaminants) and regeneration operations on resin adsorptive capacity. EvTEC contracted with Martel Laboratories, Baltimore, Maryland, to perform the analytical resin testing. The bench-scale tests were performed as follows:

- A set amount (approximately 125 ml) of both virgin and used (Column 1) resins were rinsed with de-ionized water. A total of six (6) samples were prepared - three (3) each from both the virgin and used resins.
- The resins were regenerated using a 0.5 M ZnSO<sub>4</sub>/5% H<sub>2</sub>SO<sub>4</sub> solution by adding the regeneration solution to each of the six resin samples. Approximately 0.4 liters of regeneration solution were added to each resin sample and the contents were stirred gently for 15 minutes.
- Following mixing, the regeneration solution was decanted from each resin sample and the samples were again rinsed using approximately 0.4 liters of de-ionized water. The de-ionized water was subsequently drained leaving enough solution to maintain the resin's samples completely submerged in liquid.
- Each of the resin samples were tested for adsorption capacity using stock solutions of NH<sub>3</sub>-N. The pH of the solutions were maintained in the 7.0 to 7.3 range. Both virgin and used resin samples were added to each of the standard stock solutions. The resins were gently stirred in the stock solutions to minimize liberation of free

ammonia. The contracted laboratory ran a preliminary test with no resin and only a stock solution to ensure that the ammonia was not volatilized during the resin capacity testing. Following mixing, each resin sample was drained and the concentration of ammonia in the decanted solutions were determined. The following stock solution volumes and concentrations were used: 12 liters of 200 mg/l NH<sub>3</sub>-N stock solution; 8 liters of 300 mg/l NH<sub>3</sub>-N stock solution; 5 liters of 500 mg/l NH<sub>3</sub>-N stock solution.

**Table 3-3** summarizes the results of the tests. Generally, the pilot plant's previously used resin (Column 1, which was used for the entire pilot demonstration) was found to have less sorptive capacity than the virgin resin at all concentrations and solution contact times, i.e., the resin experienced a loss in the total ammonia uptake capability. The pilot plant's resin was regenerated approximately 48 times over the course of this study. The ultimate capacity, i.e., 10 hours solution contact time, of the used resin ranged between 67 and 84% of the virgin resin capacity, with an average value of approximately 77% of the virgin resin capacity. Due to the fact that this study is based on the testing at one individual site and from data obtained over an operating time of approximately 3 months, the reader is cautioned against inferring either of the two following factors from the data:

- The rate at which the media loses capacity from the virgin resin condition; and,
- The practical lower end bound on the media sorptive capacity.

As with all new technologies, long-term operational data will be obtained through full-scale implementation of the ARP system, but this future testing is beyond the scope of this verification effort.

## 3.6 Crystal Growth and Dusting

ThermoEnergy and FWENC provided the crystal yield data for this EvTEC verification effort. The crystal values were not field verified by EvTEC or the EvTEC Evaluation Panel. ThermoEnergy and FWENC are bound by their signed disclosure statements to provide factual and accurate data for this EvTEC verification effort and it should be treated as supplemental information. FWENC was able to produce

<b>Initial Ammonia Concentration = 200 mg/L</b>			
	5 Minutes	1 hour	10 hours
Virgin Resin	4.80	7.10	8.06
Column 1 Resin	4.80	5.76	6.72
<b>Initial Ammonia Concentration = 300 mg/L</b>			
	5 Minutes	1 Hour	10 Hours
Virgin Resin	8.32	8.96	9.60
Column 1 Resin	5.76	6.40	6.40
<b>Initial Ammonia Concentration = 500 mg/L</b>			
	5 Minutes	1 Hour	10 Hours
Virgin Resin	6.80	7.20	7.60
Column 1 Resin	3.60	3.60	6.40
<b>Average Capacity for All Initial Concentrations</b>			
	5 Minutes	1 Hour	10 Hours
Virgin Resin	6.64	7.75	8.42
Column 1 Resin	4.72	5.25	6.50

**Table 3-3. Media Sorptive Capacity \***

**\* All sorptive capacities are in units of grams NH<sub>3</sub>-N per liter of resin.**

approximately 162.1 lb (73.5 kg) of ammonium-zinc sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> • ZnSO<sub>4</sub> crystals from 11,717 gallons (44,350 liters) of centrate flow processed in the ARP. The ammonium-zinc sulfate crystal amount listed above was produced during the pilot plant operations starting November 1, 1998, and ending December 5, 1998. Pilot plant operations were more representative after October's polymer and ferric chloride overdose occurrences and as a result, mass balance calculations were not performed on data obtained earlier than November 1, 1998. After October 1998, three mass balance closures were achieved and calculated for 18 production runs and FWENC measured approximately 9.63 lb and 4.67 lb of NH<sub>3</sub>-N lost to backwash and crystallization decant operations, respectively, for these production runs.

Based on FWENC's field data collection (see Table 3-4), the amount of ammonium-zinc sulfate crystals (i.e., intermediate

crystals) produced ranged from 36.8% to 72.5% of the theoretical yield. Overall the ratio for the three mass balances was approximately 46.9% of the cumulative theoretical yield value of 345.7 lb (156.9 kg). The highest yield, 72.5% was achieved for the last mass balance and according to FWENC, the crystallization process improved as the pilot process progressed. FWENC was able to close mass balances from the concentrated regeneration solution to the crystallization process for ammonia and zinc at 84.4% and 84.2%, respectively. These values are based on three mass closure events. More detailed information on the calculations and this data can be obtained from ThermoEnergy and FWENC. FWENC believes it is realistic to obtain mass balance closure values of 85-95% of the ammonia initially present in the concentrated regeneration solution and removed during crystallization process. The ammonia should be accountable in the forms of vaporized ammonia sent to the final crystallization process,

Production Run	Field Crystal Weights (lbs.) for (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ZnSO <sub>4</sub> (i.e., Intermediate Crystals)		Theoretical Yield Calculations (lbs.) for Intermediate Crystals	
	Wet Crystals	Dry Crystals	Dry Crystals	Ratio (%)
First Mass Balance	90.0	69.3	164.4	42.1
Second Mass Balance	56.0	40.0	108.5	36.8
Third Mass Balance	62.2	52.8	72.8	72.5
Pilot Plant Totals	NA	162.1	345.7	46.9

**Table 3-4. ARP Crystal Production \***

**\*FWENC supplied information for November through December 1998 pilot plant operations**

and the liquid ammonia left in the decant liquid from the intermediate crystallization process, which is returned to the regeneration solution tank.

Throughout the EvTEC evaluation, the final crystallization process was hampered by the pilot plant scrubber unit. The scrubber unit delivered to the site was not the unit intended for this study, and due to this difficulty with the scrubber unit, the final step in producing the ammonium sulfate crystals was not instituted until the last week of operation. According to FWENC personnel approximately 20 lb of ammonium sulfate crystals were produced from intermediate crystals in the last two mass balance processing runs. Although the total flow for these runs is known, i.e., approximately 6,476 gallons (24,512 liters) of centrate processed, no yield calculations were made. This was due to the timeframe involved (over three weeks between runs) and the open and outside field conditions in which the scrubber ammonium-rich water was stored between mass balance runs.

As can be seen in **Figure 3-4** crystal dusting did not appear to be a problem during the intermediate crystallization step. The intermediate crystals were similar to rock salt in appearance, texture, and size. The full-scale ARP system will have the final crystallization step, i.e., production of ammonium sulfate crystals (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, enclosed so that dusting and worker exposure are not concerns.

FWENC had additional off-site testing performed on the evaporation and crystallization efficiencies for the ammonium zinc sulfate produced from the ARP system. During the testing at Oakwood, FWENC shipped a 55-gallon drum of processed centrate regeneration solution to Ionics Resources Conservation Company, Bellevue, Washington. The results of this bench scale testing are available through FWENC and ThermoEnergy Corporation.



**Figure 3-4. Intermediate Ammonium-Zinc Crystals**

### 3.7 Potential for Crystallization Stream Biofouling

The intermediate crystals, through qualitative observation by FWENC and EvTEC, did not exhibit common biofouling characteristics such as slimy appearance and objectionable odors (see **Figure 3-4**). Similarly, FWENC noted no biofouling problems in the final ammonium sulfate crystals produced during the last week of the EvTEC evaluation.

### 3.8 Contaminant Effects on the Crystallization Stream

Influent contaminants, particularly cationic metals such as calcium, may be an area of concern in the crystallization steps. Iron and other contaminants exchanging for zinc on the ARP resin subsequently enter the regeneration tank following column renewal and regeneration. Given sufficient time, these contaminants will likely build in concentration in the regeneration solution. As the crystals produced during the EvTEC evaluation were not analyzed for specific impurities, no definitive statements can be made regarding their impact on the crystallization processes, but calcium, magnesium, total phosphorus and alkalinity were analyzed during the end of the pilot study to see if they were affecting the ARP columns.

Table 3-5 list the values for the additional parameters tested for during the last two days of testing. During this period, FWENC processed approximately 620 gallons (2,347) of centrate. As expected, the alkalinity is destroyed and removed with the removal of the ammonia-nitrogen. Phosphorus, calcium and magnesium appear to be taken up by the resin columns. It should be noted that these results are based on only two events and a limited amount of flow.

### 3.9 ACCUTEST® Laboratory QA/QC Summary

As mentioned throughout this report, ACCUTEST® performed the off-site laboratory analysis for this EvTEC verification effort. ACCUTEST® provided detailed technical reports for each set of analytical laboratory work that they performed over the sixteen (16) trip visits. The laboratory deliverables included the following:

- Summary sheets listing analytical results for all targeted and non-targeted compounds
- Summary table cross-referencing field ID#'s vs. lab ID#'s
- Chain of Custody forms
- Methodology Summary
- Method Detection Limits
- Conformance/Non-Conformance Summary

Statistic	12/8/99 Date (mg/L)		12/9/99 Date (mg/L)	
	Influent	Effluent	Influent	Effluent
Calcium	29.3	<5.0	28.0	<5.0
Magnesium	28.3	<5.0	31.3	<5.0
Alkalinity	1,670	<5.0	1,690	<5.0
Phosphorus-Total	28.7	2.9	32.2	5.8

**Table 3-5. Analyte Concentrations in Centrate and Column Effluent**



During the EvTEC evaluation testing there was a total of three instances where analytical results were outside method QC acceptance criteria. They were as follows:

- Sample E41050 for October 22, 1998 –Percent recovery for the Matrix Spike (MS) sample was outside of QC limits for ammonia-nitrogen.
- Sample E41293 for October 26, 1998 –Out of control results for the continuing calibration check for percent recovery QC limits for iron.
- Sample E41768 for November 7, 1998 –Out of control results for the continuing calibration check for percent recovery QC limits for iron and zinc.

None of the above situations required qualification of any data. For the ammonia-nitrogen results (E41050), qualification was not required since the spike concentration (220 mg/L) was less than 4 times the sample concentration (1100 mg/L), i.e., “4x Rule”, as described in the USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, February 1994. All iron and zinc samples were accepted without qualification as the lab certified that no environmental samples were analyzed during the excursions in percent recovery of the continuing calibration checks.

