EVALUATING AND APPLYING WHOLE EFFLUENT TOXICITY (WET) TESTING AND TIE/TRE PROTOCOLS TO IMPROVE WASTEWATER TREATMENT PERFORMANCE AND PERMIT COMPLIANCE

Louis H. Knieper[1*], Glenn Augustine[1] and Keith Pilgrim, Ph.D.[2]
[1]Southern Minnesota Beet Sugar Cooperative, P.O. Box 500, Renville, MN 56284 and
[2]Barr Engineering Company, Inc., 4700 West 77th Street, Suite 200,
Minneapolis, MN 55435

ABSTRACT

NPDES discharge permit requires passing the Whole Effluent Toxicity acute test at 100% concentration of treated effluent using fathead minnows (*Pimephales promelas)* and the water fleas (*Daphnia magna* and *Ceriodaphnia dubia).* Success was inconsistent with a 50% pass rate causing costly response activities and regulatory displeasure. Southern Minnesota Beet Sugar Cooperative (SMBSC) voluntarily entered a Toxicity Identification Evaluation (TIE) protocol which confirmed toxicity and general causes but did not identify a toxicant. Test methods had to be developed to quantitatively determine the presence of suspected toxicants. Only *Ceriodaphnia dubia* exhibited a consistent toxic response to the treated effluent. The Toxicity Reduction Evaluation (TRE) protocol immediately followed and spanned 4 years. Different data evaluation methods were employed to tease some understanding from the testing results. Treatment chemicals such as anti-foam oils and alum were found to increase toxicity and their use ceased or replacement products were employed. Testing procedures increased toxicity and modifications including CO2 head space were used. Exiting the TIE/TRE protocol presented a challenge due to lack of defined completion and was accomplished with 89% passing tests. SMBSC was able to establish a monitoring protocol and prediction model for the complex toxicity associated with the treated effluent discharge. Total Dissolved Solids, Potassium, Ammonia and Carbonate solubility are the synergistic causes of toxicity.

BACKGROUND

Southern Minnesota Beet Sugar Cooperative has operated a sugar beet processing facility in Renville, Minnesota since 1972. The Factory and Wastewater Treatment Plant were expanded in the late 1900's to its present configuration. The NPDES/SDS Permit was completely rewritten and reissued in 2004 to accommodate the increased demands resulting from doubling beet processing capacity. This permit survives unaltered today. Discharge is allowed on a seasonal basis from September through March. A variance allows for the treated effluent to exceed the stringent dissolved mineral requirements of the State of Minnesota. SMBSC's discharge is the headwaters of a drainage ditch that is an extension of the East Fork of Sacred Heart Creek and as such the permit does not allow for in stream dilution to meet discharge requirements. Sacred Heart Creek is a tributary of the Minnesota River, part of the Minnesota River Basin and Lake Pepin TMDL's and the last 2.5 miles is considered a spawning area for certain fish species.

The NPDES Permit has limits and conditions that are designed to protect the potential uses for the extended waterway. SMBSC has had exceptional success with offsetting phosphorous discharge through trading and applying cover crop credits. EPA and various waterway protection groups have recognized the pioneering efforts of SMBSC in this pollutant trading arena. Through the efforts of municipal and industrial users over the last 12 years, the Minnesota River has exceeded expectations and achieved the Dissolved Oxygen goal ahead of schedule due to phosphorous reductions.

To obtain the variance in the NPDES/SDS Permit, SMBSC accepted effluent toxicity testing as a permit compliance limit and conducts Acute Whole Effluent Toxicity tests on a routine basis. The effluent must exhibit a TUa of less than 1 to be considered acceptable. TUa is the reciprocal of the LD50 concentration at 100% effluent exposure. Stated differently, more than 50% of the test organisms in each of the three test species must survive acute exposure at 100% effluent concentration. This has presented some non-compliance events for SMBSC. The toxic response was not consistent, predictable or routinely related to monitored effluent parameters but, tests were failed more than 60% of the time. SMBSC entered Toxicity Identification Evaluation and Toxicity Reduction Evaluation (TIE/TRE) protocols in 2006 completing the effort in 2012. In 2013, 100% of the WET tests have met or bettered permit required TUa levels. This paper is presented to show how the information obtained has been translated in to operational changes and prediction models that improve not only NPDES/SDS compliance but also enhance the environmental stewardship at SMBSC.

WASTE WATER TREATMENT SYSTEM

SMBSC employs two wastewater treatment technologies in its system, Land Application and a Waste Water Treatment Plant. Land application (spray irrigation) is common for food processing facilities which have wastewater that is contaminated predominantly with simple organic compounds, nutrients and minerals. The soil matrix is used to contain and treat the wastewater as it percolates through the root zone. Microbes break down components which are taken up by vegetation that is then harvested. SMBSC grows hay on the 950 acres dedicated to spray irrigation of wastewater. Rotating pivots, travelling pivots and travelling guns are used to apply the wastewater to hay land. Hay is harvested and sold for feed. SMBSC land applies about 130 million gallons of wastewater each season.

Wastewater is stored in ponds on the site and blended for treatment in a biological treatment plant. Clay lined ponds store high strength wastewater, low strength wastewater and recycled condensate (about 450 million gallons capacity) and treated effluent (45 million gallons capacity). Ponds provide cooling, settling, recycling, segregation and equalization of wastewater and allow SMBSC to blend for optimum performance. Treatment options include anaerobic digester and/or aerobic basins followed by clarification, filtration and disinfection.

The treatment plant capacity is more than 2.5 million gallons per day but the permit limit is 2.3 million gallons per day or 483 million gallons per season. The treated water pond allows for extended operation if necessary to maintain storage capacity and factory operations. Discharge is not allowed during fall and spring flooding or when ice or snow blocks the waterway. This restriction can cause an annual 30-40 million gallon decrease in allowed discharge. SMBSC was generating about 160 gallons of wastewater per ton of beets sliced on about 2.8 million tons of beets or about 450 million gallons of wastewater per year. Storm water may not be discharged at SMBSC and precipitation can account for 50 to 80 million gallons of additional wastewater. This crude water balance is indicative of the slim margin for error in the Wastewater Treatment System

WET TESTING AND TIE/TRE RESULTS

WET tests in 2005 and 2006 highlighted the inconsistent performance of the Wastewater Treatment System with intermittent toxic responses. The initial evaluation showed a correlation of toxicity with elevated ammonia concentrations in the effluent. Nitrification in the treatment process was linked to aerobic basin temperature and operators responded to keep the basins above 15^0 C. Toxicity persisted and the TIE was initiated. Local, national and research laboratories were utilized in an intensive forensic search for a toxicant. SMBSC and SPRI developed new procedures to identify and quantitatively measure Saponins in wastewater. No single or specific chemical toxicant was identified. SMBSC did determine that the use of siloxane based foam suppressing chemicals in the wastewater treatment plant could pose a risk of toxicity in the effluent and alternative chemicals were obtained. With no toxicant identified, SMBSC also initiated the toxicity reduction research. The parallel applications of these two lines of inquiry lead to significant findings that helped to improve the opportunity to reduce toxic response.

The first major finding was that the toxicity test procedure enhanced the effluent toxicity. Regulatory officials were reluctant to accept this fact and the likelihood of modifying an EPA standard procedure was not encouraging. Wastewater samples are collected, stored and shipped at 4^0C but tested at 25^0C. Treated wastewater and local surface waters are high in bicarbonate. When the refrigerated samples are warmed for the testing, calcium carbonate precipitates and CO2 is released. This causes the test solution pH to rise during exposure. SMBSC was able to demonstrate that a pH rise of 1 SU during the toxicity test was likely to cause >50% mortality (failed test) of *Ceriodaphnia dubia* (Figure 2). Regulators allowed CO2 headspace application to control the pH drift and minimize this toxic response

With this knowledge, SMBSC saw an opportunity to further improve the potential to pass a WET test by changing the treatment plant procedures. Treated wastewater is pumped through a mile and one-half pipeline to the waterway. The high calcium and bicarbonate in the treated effluent caused scaling so Sulfuric Acid was added to the effluent to keep the pH just under 7.0 SU. This addition was stopped and the effluent pH stabilized between 7.5 and 8. An additional benefit was realized as a decrease in low level mercury concentration. Mercury was a trace contaminant in the Sulfuric Acid. Final filtration and transfer equipment require more frequent descaling and rotation of in-service pumping equipment is necessary to maintain discharge capacity.

SMBSC soon discovered that aluminum in the effluent could be toxic to Daphnids. The potential was considered in 2006 but, the concentrations found in the effluent were believed to be well below the toxic response reported in the literature. The connection between aluminum and Daphnid toxicity was observed in pilot and bench scale tests while trying to control bicarbonate in the effluent. Extensive testing was conducted at unit discharges throughout the treatment plant. A marked increase in toxicity was observed after the addition of Alum in the Secondary Clarifiers to remove phosphate from the treated wastewater stream. Standard addition of alum in actual and synthetic effluent waters followed by toxicity tests with *Ceriodaphnia dubia* confirmed the toxic response. SMBSC and BARR concluded that the toxicity of aluminum increased as treated effluent specific conductance increased and that the toxicity of aluminum was increased by the presence of sulfuric acid. SMBSC ceased using Alum and switched to Ferric Chloride as the phosphate control chemical.

From 2009 through 2011 the frequency of toxicity testing increased and sampling was extended through the operating units in the wastewater treatment plant. The acute toxicity concern was limited to only one species, *Ceriodaphnia dubia,* which decreased the time and costs of evaluation. Sampling and testing were conducted on a bi-weekly then weekly schedule that encompassed the entire discharge season and continued as the treatment plant processed wastewater for summer use. With the identified causative agents under control, toxicity occurred less frequently. The next culprit was identified as potassium which is extracted from the beets and possibly soil entering the washers. The toxic response of *C. dubia* to potassium concentration was so subtle that it had been masked by other components that were no longer in the treated effluent. Toxicity of potassium in the treated effluent was at times well below the concentrations found in the literature. Further evaluation of the data implied that the SMBSC treated effluent toxicity was a result of synergistic effects between dissolved solids (Specific Conductance), Ammonia, Potassium and Alkalinity. A regression model was developed in 2012 by Dr. Keith Pilgrim, Barr Engineering Company, that accounted for the synergy of all of the tested components (Figures 3A & 3B).[1]

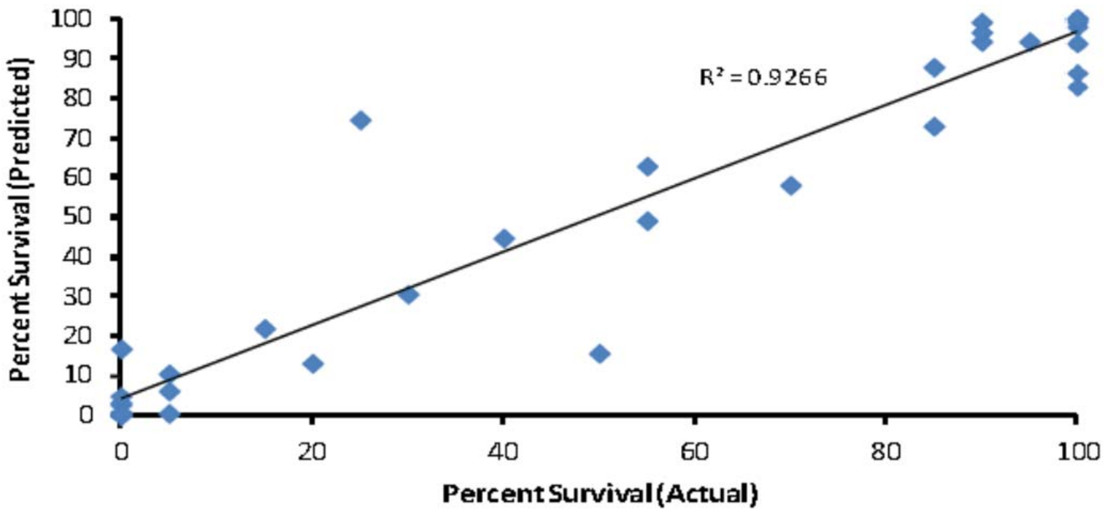
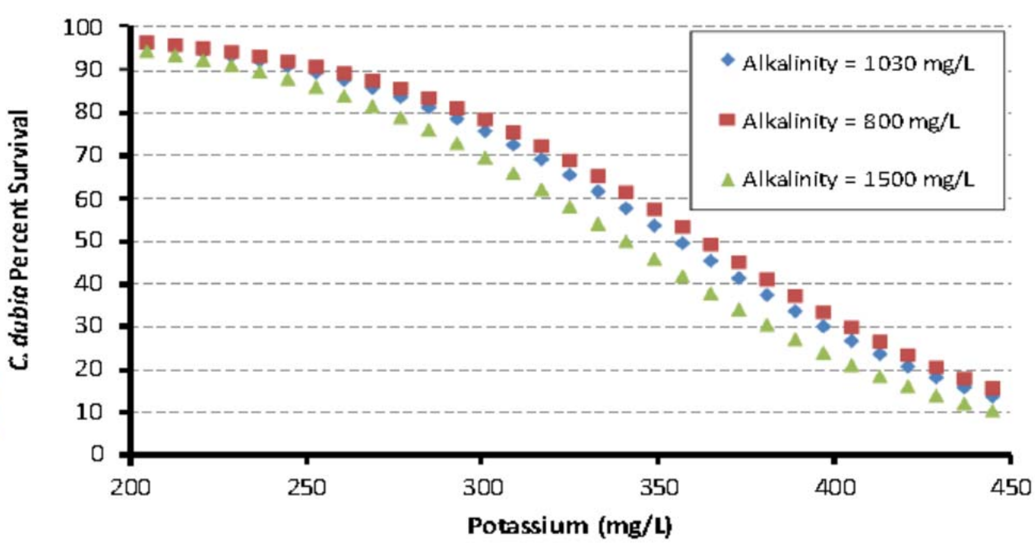


Figure 3A: Demonstration of model accuracy of a logistic regression based upon acute WET tests without carbon dioxide headspace and with a range of potassium doses added to induce toxicity from high levels of potassium. The regression model included most of the monitored waste water constituents and is as follows: *Percent Survival* = 100*1/(1 + exp(-(8.685- 0.001*Alk+0.004*Cl-0.956*NH_4-N+0.015*SO_4+1.008*Al -0.020*K-0.008*K))). All units in the model are milligrams per liter.



[1] Keith
Southe

Figure 3B: Estimated *Ceriodaphnia dubia* survival in acute WET tests for a range of potassium concentrations and three alkalinity levels in SMBSC Post Air effluent. Estimates are based upon the outcome of a regression model which included acute WET tests with *C. dubia* and no carbon dioxide headspace.

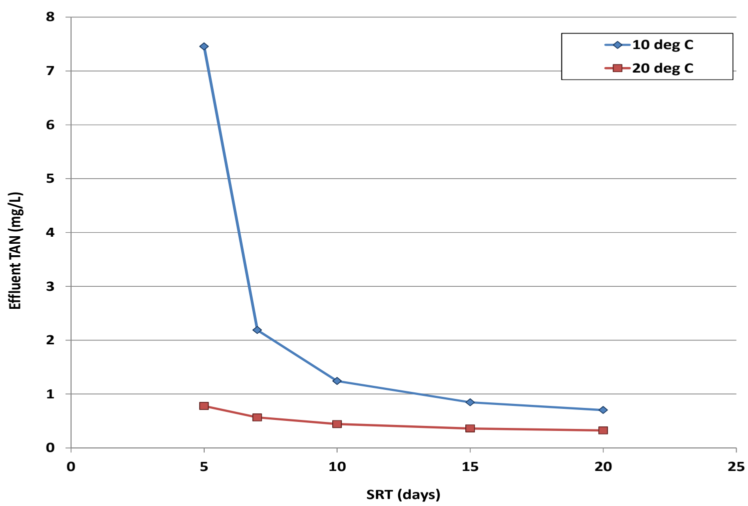
The model allowed SMBSC to evaluate the impact of each component and establish a plan to minimize toxicity. Potassium in the wastewater is strictly from the sugar beet tissue. Soil was thought to contribute but, based on the extensive analytical efforts; the soil in the beet wash water does not contribute to the effluent potassium. Solids removed from the wash water loop are consistently several times higher in potassium concentration that the beet fields and Tare 1 soil by-product. Elimination of potassium will require major modifications to the factory operations and is a long range goal. SMBSC had reduced some of the toxicants down to minimum levels (aluminum, sulfate, and alkalinity) and addressed the pH rise in the WET test protocol (CO_2 headspace testing). The focus was to optimize treatment to control ammonia in the wastewater plant effluent.

During February 2013, SMBSC observed a mild toxic response of *Ceriodaphnia dubia* to an increase in several parameters – Alkalinity, TDS, Specific Conductance and TSS (Turbidity). While none of the parameters independently exceeded their threshold for toxic response in SMBSC treated discharge, the increase across several parameters was reflected in some mortality during the toxicity scan test. The influence of suspended solids (turbidity) is a new development. This correlation was also occurring over the winter in other wastewater treatment plants but the relationship has not been thoroughly studied. The toxic mechanism may be simply an accumulation of particulates on the test organisms which reduces buoyancy and causes the individuals to sink. While not dead, the WET test protocols require that these individuals be counted as deceased. SMBSC does not plan to conduct further testing to develop any correlations between TSS or Turbidity and mortality in WET tests. Improved filtration was already part of the treatment plant improvement plan.

AMMONIA CONTROL

Barr Engineering conducted an evaluation of the wastewater treatment plant at SMBSC to optimize the facility and provide direction for improvements to meet the larger harvests predicted at SMBSC. The first improvement identified was adequate heat to sustain biological community and allow the complete conversion to nitrogen. SMBSC operates their WWTP through the coldest months of the year. The facility is designed to obtain heat from waste energy and additional heat exchange capacity was installed. Additional heat and a more reliable and consistent source was necessary so SMBSC converted Biogas Boilers to also burn Natural Gas and installed a supply pipeline last year. Increased steam availability (new boiler) at the factory will further improve the waste heat availability for the WWTP. The combined benefits to power, production and compliance provided justification for the new equipment.

Barr Engineering also conducted modeling evaluations to determine the optimum operating conditions that provided the best opportunity for ammonia control at the WWTP. Steady state evaluation used the approach described by the US EPA. [2] The approach allows the calculation of treatment capacity (effluent total ammonia concentration) for a fixed set of solids retention time (SRT), temperature and pH conditions. Using rate functions established in the 2010 EPA Manual, analytical data gathered during the TIE/TRE investigations and WWTP design parameters, it was apparent that under normal operating conditions (no biocides, sufficient nutrients, alkalinity and DO available) the SRT must be greater than 10 days to assure no ammonia impact on the WET test toxicity (effluent TAN<6mg/L). The importance of maintaining correct operating temperature in the Aerobic Basins is also dramatically displayed.



A more elaborate evaluation was conducted using a state- of- the- art activated sludge modeling program developed by EnviroSim known as PetWin+ version 3.1 built on an ASDMi model. [3] Multiple parameters of plant operation can be modeled simultaneously in a dynamic scenario to identify key control components. The model was run based on the available operating and analytical data collected at SMBSC from 2006 – 2011 and industry accepted standards. The results of numerous dynamic model runs at a variety of loading and operating conditions demonstrated that load management, temperature and SRT control are necessary to prevent Ammonia breakthrough and WET test failure.

---

[2] US EPA, 2010; “Nutrient Control Design Manual EPA/600/R-10/100”

[3] EnviroSim Associates, Limited, 2011; “PetWin+ Help Manual”

TKN 100 mg/L

		SRT (d)			
		10	20	40	60
Temp (degC)	10	1.7	0.9	0.6	0.5
	15	0.8	0.5	0.4	0.4
	20	0.5	0.3	0.3	0.3

TKN 150 mg/L

		SRT (d)			
		10	20	40	60
Temp (degC)	10	9.9	2.1	1.3	1.1
	15	1.8	1.0	0.7	0.6
	20	0.8	0.6	0.4	0.4

TKN 200 mg/L

		SRT (d)			
		10	20	40	60
Temp (degC)	10	35.9	6.2	2.6	2.0
	15	4.0	1.5	1.0	0.9
	20	1.2	0.8	0.6	0.6

TKN 250 mg/L

		SRT (d)			
		10	20	40	60
Temp (degC)	10	74.4	21.7	4.2	4.0
	15	11.7	2.3	1.5	1.2
	20	1.7	1.0	0.8	0.7

These evaluations provided the parametric limits for optimum WWTP operation to control ammonia:

- Monitor and blend to control influent ammonia and TKN concentrations
- Maintain Aerobic Basin temperature above 15^{0}C
- Maintain SRTs greater than 20 days

SMBSC has committed the capital to improve the physical plant to meet the conditions required for optimum ammonia control. WWTP operating parameters and procedures are established, taught and tracked to assure compliance with the minimum SRT in the aerobic basis. Ammonia has not returned as a toxicant.

SUSPENDED SOLIDS CONTROL

SMBSC uses clarifiers and sand filters to remove suspended solids after treatment. Ferric chloride and polymer are added at the inlet to the secondary clarifiers to enhance solids separation. Effluent is filtered through sand filters to remove remaining suspended particulates. Over the last two seasons, SMBSC has been conducting full scale tests of rotary cloth filters to augment or replace the sand filters. The rotary cloth filters provide equal or better solids removal with less maintenance and downtime. Additional units will be installed as part of the treatment plant improvements.

POTASSIUM CONTROL

For several years the soil washed from sugar beets was considered a source of potassium. Testing conducted during the TIE/TRE evaluations indicated that the wash loop mud was a potassium sink. The potassium in wastewater is derived from the sugar beets. SMBSC has reduced wash loop blow down and has generally maintained potassium in the treated effluent below the 350 mg/L level that is toxic to Daphnids.

TERMINATION OF TIE/TRE

The Minnesota Pollution Control Agency and Minnesota State Rules do not identify the end of the TIE/TRE Protocol. EPA does provide guidance and protocols for entering a TIE/TRE program but, no guidance was found to end the intensive testing.

As a practical approach to determining if a TRE is an appropriate response, EPA recommends if toxicity is repeatedly or periodically present at levels above the effluent limits more than 20 percent of the time, a TRE should be required. [4]

SMBSC had to define and negotiate an end to this costly and time consuming project. The regulatory agencies accepted the position that if a 20 percent failure rate of toxicity testing starts the TRE, an 80 percent passing rate should cause termination of the TRE. SMBSC exceeded this standard in the 2011-2012 discharge season. The end game consisted of extended toxicity assurance testing over the 2012 – 2013 season with Quarterly WET tests and monthly *Ceriodaphnia dubia* scans (Figure 4).

SUMMARY

SMBSC has established a well-defined response plan to assure compliance with WET testing as a NPDES/SDS discharge permit limit. Through the toxicity testing and evaluation protocols, detrimental activities were identified and terminated. Precise and appropriate facility improvements were identified and prioritized to meet the company operating demands and capital limitations. Benefits of each component in the compliance assurance plan could be quantified and presented to regulatory agencies for review and acceptance. The extensive data collection required for the TIE/TRE effort was further used to improve the standard operating procedures within the wastewater treatment system. Key indicators were identified and monitoring protocols were enhanced. The newly developed protocols provide adequate time to respond, proper adjustment procedures and clarification of acceptable operating limits. The potential for compliant and successful operation of the wastewater treatment system has been enhanced. The seven year effort has improved SMBSC's insight into critical interfaces between factory operations and treated effluent compliance.

[4] US EPA, 1991; "Technical Support Document for Water Quality-based Toxics Control" page 118.

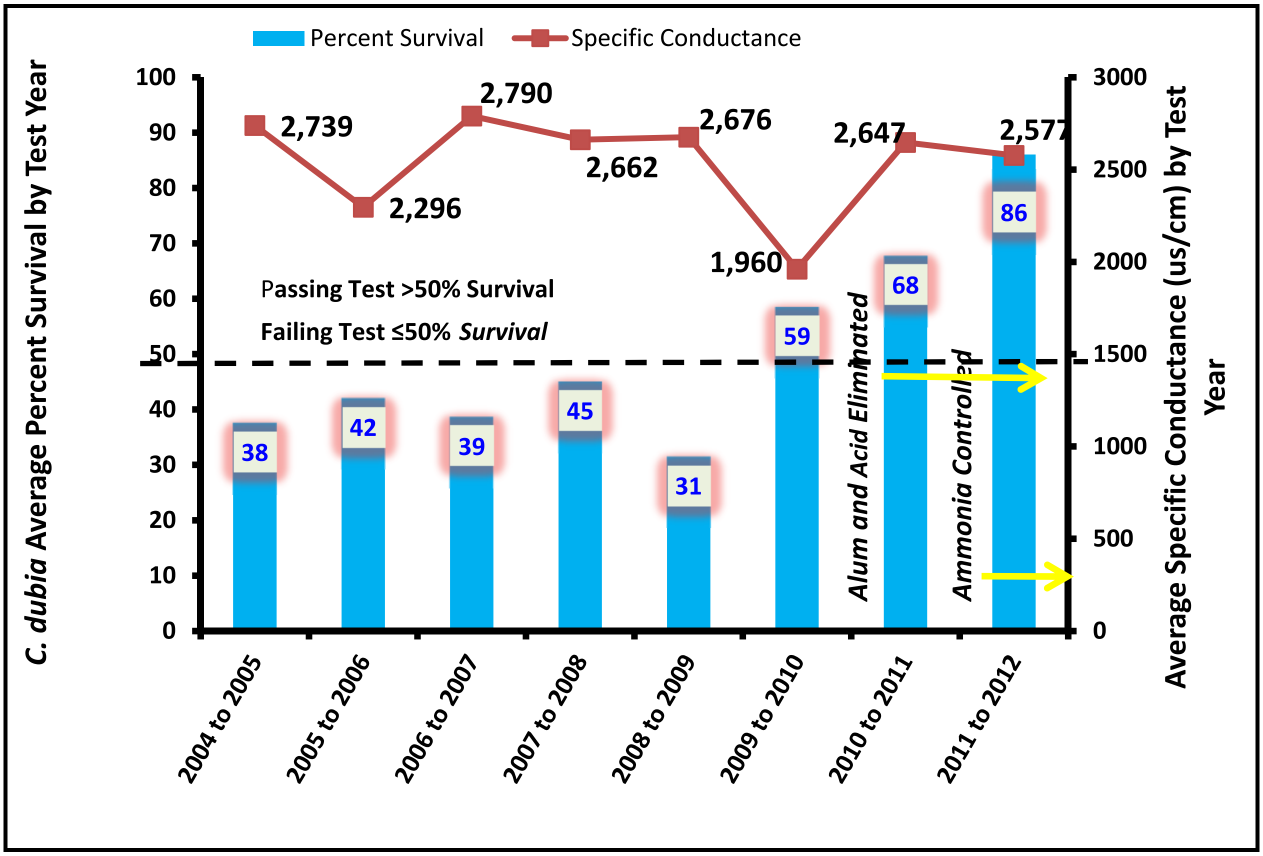


Figure 4: SMBSC toxicity reduction and TIE/TRE termination. From Barr Report"2011 to 2012 Toxicity Identification/Reduction Evaluation Study on Southern Minnesota Beet Sugar Cooperative Effluent", June 2012.