Treatment of a Duke Energy Power Plant wastewater by Thermal Evaporation: a review

By

Leanne Wilson

In partial completion of the
Master of Environmental Assessment

May 2022

Abstract

Wilson, Leanne. Master of Environmental Assessment. Treatment of a Duke Energy Power Plant wastewater by Thermal Evaporation: a review

Water resources are an integral part of providing industries, especially electric generating facilities the ability to operate. A downside is the amount of wastewater that is produced. With the adoption of North Carolina's Clean Smokestack Act and National Air Quality standards on SO2 emission into the atmosphere, many fossil fueled plants have converted their facilities with FGD or Flue Gas Desulfurization systems in order to "scrub" the SO2 from their emission sources. Having to clean up one medium, the air, introduced new opportunities to create wastewater. Under the Clean Water Act, facilities that generate wastewater are responsible for adhering to the facility's National Pollutant Discharge Elimination System or NPDES permit. With the conversion to FGD, a Duke Energy facility installed the use of a Bioreactor system that uses heterotrophic bacteria to reduce pollutants in the wastewater. Problems arose with increased concentrations of metals, i.e., Selenium, Mercury, Boron, Thallium and Manganese that were not meeting the facility's NPDES limits. After a special order of consent was issued by NCDEQ and a 3rd party wastewater study conducted, the decision was made to seek new FGD treatment technologies by Duke Energy to comply with the NPDES limits of the receiving waterbody. The treatment that was selected was the Zero Liquid Discharge (ZLD) or Thermal Evaporating system. In the years following the commissioning of the ZLD, there has been significant improvements to the water quality and chemistry of the discharge coming from the plant into the receiving reservoir. All metals of concern decreased with Selenium at 94.81%, Mercury at 93.21%, Boron at 64.88%, Thallium at 50.43 % and Manganese at 68.79%.

Biography

Leanne Wilson was born and raised in Roxboro, North Carolina. She received her undergraduate degree from North Carolina State University with a major in Environmental Technology and a minor in Environmental Toxicology in December 2009. In the fall of 2014, she was employed as a contingent worker for Duke Energy as a Chemistry Tech responsible for water pre- and post-treatment in the operation of one of their coal-fired power plants. In May of 2018 she was hired as a full-time Senior Environmental Specialist with Duke Energy where she is responsible for maintaining the compliance of the station's various environmental permits, i.e., Title V Air Permits, NPDES Permits, and ensuring the environmental safety of the station. She holds several wastewater licenses including Biological and Physical-Chemical for the state of North Carolina. Along with working full-time with Duke Energy, Leanne began pursuing her master's in Environmental Assessment in early 2018 with plans to graduate in the Spring of 2022.

Acknowledgements

I would first like to thank the faculty and staff of the Environmental Assessment program and especially Mrs. Linda Taylor for her time and patience in advising me throughout my college career. I first was introduced to Mrs. Taylor in my undergraduate years, and she was an integral part in defining my professional career with her teaching and advising. It has been a great learning experience to continue to work with her since pursuing my master's degree in Environmental Assessment and I wish her the best of luck on her retirement in June 2022. I would also like to thank the personnel of Duke Energy and the Natural Resources department within Duke Energy for providing the information for this analysis. I would like to thank my manager at Duke Energy, Steven Connor for allowing me to pursue my master's and encouraging me professionally. Finally, I would like to thank my husband Jacob and 3 children for their patience, love, and support in pursuit of my degree during these last 4 years.

Table of Contents

List of Terms

B: Boron

CAA: Clean Air Act

CTBD: Cooling Tower Blowdown

CSA: Clean Smokestacks Act

CWA: Clean Water Act

DMR: Discharge Monitoring Report

EPA: Environmental Protection Agency

FGD: Flue Gas Desulfurization

GAC: Granulated Activated Carbon

Hg: Mercury

Mn: Manganese

NAAQS: National Ambient Air Quality Standards

NCDEQ: North Carolina Department of Environmental Quality

NCSWQS: North Carolina Surface Water Quality Standard

NPDES: National Pollution Discharge Elimination Standard

Se: Selenium

SO2: Sulfur Dioxide

SOC: Special Order of Consent

Tl: Thallium

ZLD: Zero Liquid Discharge

1. INTRODUCTION

Fossil-fuel generation facilities are subject to numerous types of environmental regulations. These facilities must meet compliance in various media including the air and water. In North Carolina , The Clean Smokestacks Act, officially titled the Air Quality/Electric Utilities Act (SB 1078), requires significant actual emissions reductions from coal-fired power plants in North Carolina. The act differs from federal rules, which allow utilities to buy pollution credits from other states instead of cutting air pollution from power plants in state (NCDEQ, 2001). Under the act, North Carolina's utilities must reduce actual emissions of nitrogen oxides (NOx) from 245,000 tons in 1998 to 56,000 tons by 2009 (77% reduction). Utilities also must reduce actual sulfur dioxide (SO2) emissions from 489,000 tons in 1998 to 250,000 tons by 2009 (49% reduction) and 130,000 tons by 2013 (73% reduction). This represents about a one-third reduction of the total NOx emissions and a one-half reduction of the total SO2 emissions from all sources in North Carolina (NCDEQ, 2001).

Federally, The NAAQS (National Ambient Air Quality Standard) for SO2 had a proposed revision by the EPA in 2009 and with that would reduce the amount of SO2 emitted into the atmosphere (EPA, 2009). Specifically, EPA proposed to establish a new 1-hour SO2 standard within the range of 50–100 parts per billion (ppb), based on the 3- year average of the annual 99th percentile (or 4th highest) of 1-hour daily maximum concentrations. The EPA also proposed to revoke both the existing 24-hour and annual primary SO2 standards. (EPA, 2009).

Under water regulations, The Clean Water Act prohibits any facility from discharging "pollutants" through a "point source" into a "water of the United States" unless they have an NPDES (National Pollution Discharge Elimination System) permit. The term “water of the United States “(WOTUS) is also defined very broadly in the Clean Water Act after 25 years of litigation. It means navigable waters, tributaries to navigable waters, interstate waters, the oceans out to 200 miles, and intrastate waters which are used: by interstate travelers for recreation or other purposes, as a source of fish or shellfish sold in interstate commerce, or for industrial purposes by industries engaged in interstate commerce (EPA, 2022). Duke Energy and its facilities maintain NPDES permits issued by the State of North Carolina or applicable states in which these facilities reside. These permits allow the facility to discharge into the receiving stream. The permits provide discharge limits for certain chemicals based on the receiving water body. The limits are determined based on the water quality standards of that area (NCDEQ, 2022). Metals that are discharged from these fossil fuel plants must meet North Carolina Surface Water Quality Standards as well as the proposed NPDES Permit.

In order to comply with The Clean Smokestacks Act and with the Clean Water Act, fossil-fuel generating plants have typically installed Flue Gas Desulfurization or FGD technologies to reduce the SO2 that was emitted as well as an additional wastewater treatment system to clean FGD wastes that are discharged.

FGD technologies come in a variety of scrubber systems that “scrub” the SO2 out of the emissions. These scrubbers can be wet, spray dry or dry and are capable of reduction efficiencies in a range of 50%-98% (EPA, 2003). The highest efficiency of these systems are wet scrubbers at 90% and will be discussed in this review.

With the installation of wet scrubbers at fossil-fuel power plants, constituents that were once a concern for the air are now changed by chemical reactions to fall out in the form of wastewater. There is also a byproduct of Gypsum that is formed during the chemical reaction of Limestone and SO2. Figure 1 describes the wet scrubber process and how the flue gas moves through the system (Power, 2018).

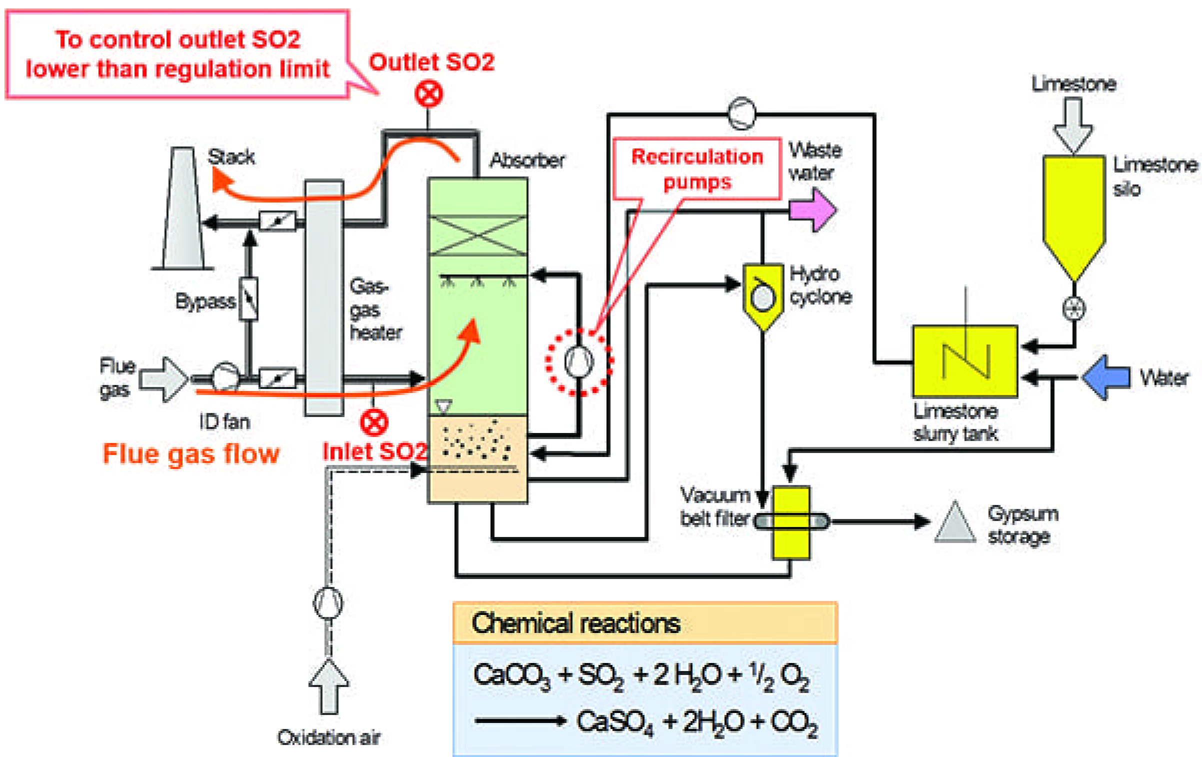

Figure 1: Flue Gas Wet Scrubber Flow Diagram. ***Courtesy of Power Magazine***

The wastewater that is generated from the wet scrubbing FGD process must be treated before it is released into the surface water. As mentioned previously, the National Pollution Discharge Elimination System or NPDES, requires limits on the constituents of the wastewater before being discharged to the receiving stream depending on water quality standards in the area (Water Tech, 2006). Parameters that are regulated by the NPDES for

FGD wastewater are typically BOD, TSS, heavy metals, selenium, arsenic, boron, temperature, pH, and TDS. At the Duke facility, wastewater from the FGD process is combined with other plant wastewater including cooling tower blowdown, steam condensate and other process waters (Water Tech, 2006). Not only must the facility meet NPDES limits, but Duke Energy must also meet the NC Surface Water Quality Standards of metals as well as shown in Table 1.

Metal	NC Surface Water Quality Standard
Selenium	5 ug/L
Mercury	0.012 ug/L
Boron	750 ug/L
Thallium	0.24 ug/L
Manganese	200 ug/L

Table 1: North Carolina 15A NCAC 02B Water Quality Standards for Surface Waters for Se, Hg, B, Tl & Mn. ***Courtesy of North Carolina Department of Environmental Quality***

Before being discharged to the receiving stream, wastewater from this process is sent to a settling pond before moving to a FGD treatment system. The exact process in which FGD wastewater is treated is dependent upon the pollutants in the water. These treatments include chemical, physical, and biological treatment that reduces and removes the pollutants that accumulate during the FGD process. The most common form of treatment of FGD wastewater is the biological processes that use specific bacteria to attack individual pollutants. Another form of treatment is that of the chemical matter known as Zero Liquid Discharge (ZLD) or Thermal Evaporation (Yaqub et al., 2019).

The ZLD system has been shown to be a sustainable wastewater treatment option by minimizing the contaminated discharge of wastewater to the receiving waterbody (Yaqub et al., 2019). As Yaqueb et al. (2019) states it is a system that consists of a variety of advanced water treatment technologies aimed at improving water usage efficiency and resource recovery. By implementing the ZLD technology, it allows the recovery of the water resource to get the most out of water recycling (Mohammadi et al., 2021). In most ZLD systems, the main driver is thermal processes. The wastewater is fed to a brine concentrator for evaporation and then a brine crystallizer. The collected distillate is then reused, and the recovered solids are either disposed of or reclaimed as valued byproducts (Yaqueb et al., 2019).

2. Flue Gas Desulphurization infancy at a Duke Energy Facility

In 2008, prior to the commissioning of the Flue Gas Desulphurization system at the Duke Energy facility, a study on wastewater was conducted to profile the receiving stream and characterize the waste that would accumulate in the settling pond (Duke Energy, 2020). The study concluded that the best type of wastewater treatment for the fossil-fuel station was a Bioreactor. In 2009, the FGD Scrubber, Settling Pond and Bioreactor were built on location at the facility's site. The Bioreactor had its own internal outfall, where it then discharged into a final outfall to the receiving stream. The NPDES permit limits that were given to the station in 2009 lists the parameters and limits to each parameter at the final outfall 002 in Table 2.

There are many metals that were monitored at this time and the main metals of concern were Mercury, Boron, Thallium, Manganese, & Selenium.

2009 – NPDES: Outfall 002 with FGD wastewater

PARAMETER	LIMITS		
	Monthly Average	Weekly Average	Daily Maximum
Total Selenium			3.8 lbs/day
Total Mercury			0.012 µg/L
Total Arsenic	10.0 µg/L		10.0 µg/L
Total Cadmium	2.0 µg/L		15.0 µg/L
Total Chlorides	672.0 mg/L		860.0 mg/L
Total Fluoride		1.8 mg/L	
Total Lead		25.0 µg/L	33.8 µg/L
Total Manganese		200.0 µg/L	
Total Barium		1.0 mg/L	
Total Thallium		0.35 µg/L	
Total Vanadium		24.0 µg/L	
Total Antimony		5.6 µg/L	
Total Boron		750.0 µg/L	
Total Cobalt		65.0 µg/L	
Total Molybdenum		170 µg/L	

Table 2: 2009- NPDES Outfall 002 with FGD wastewater. ***Courtesy of Duke Energy***

2.1 Bioreactor Technology

In the Bioreaction process, there is a down-flow granulated activated carbon or GAC packed bed reactor that has a mixture of proprietary blends of microbial strain. The GAC supports the reduction of selenium oxyanions as well as nitrate, sulfate, and other oxyanions by growing biofilm that consists of proprietary seeded bacteria (Citulski et al, 2016). A carbon source is added to the upfront process of the bioreactor because of the deficiency of organic carbon for heterotrophic bacteria growth in selenium-laden wastewater. Backwashing is the last step to remove the nitrogen gas that is generated during denitrification. It is also done to remove biofilm and solids and is an integral part of the process (Citulski et al, 2016). In the biological selenium removal process the soluble selenate and selenite are converted to elemental selenium under anaerobic conditions which are then deposited within the biofilm matrix and then removed through backwashing. The process continues and selenium reducing bacteria increase, thus removing the elemental selenium from the wastewater (Citulski et al, 2016). Figure 3 shows the GE ABMet system, which is similar to that of the technology at the Duke Energy fossil-fuel facility.

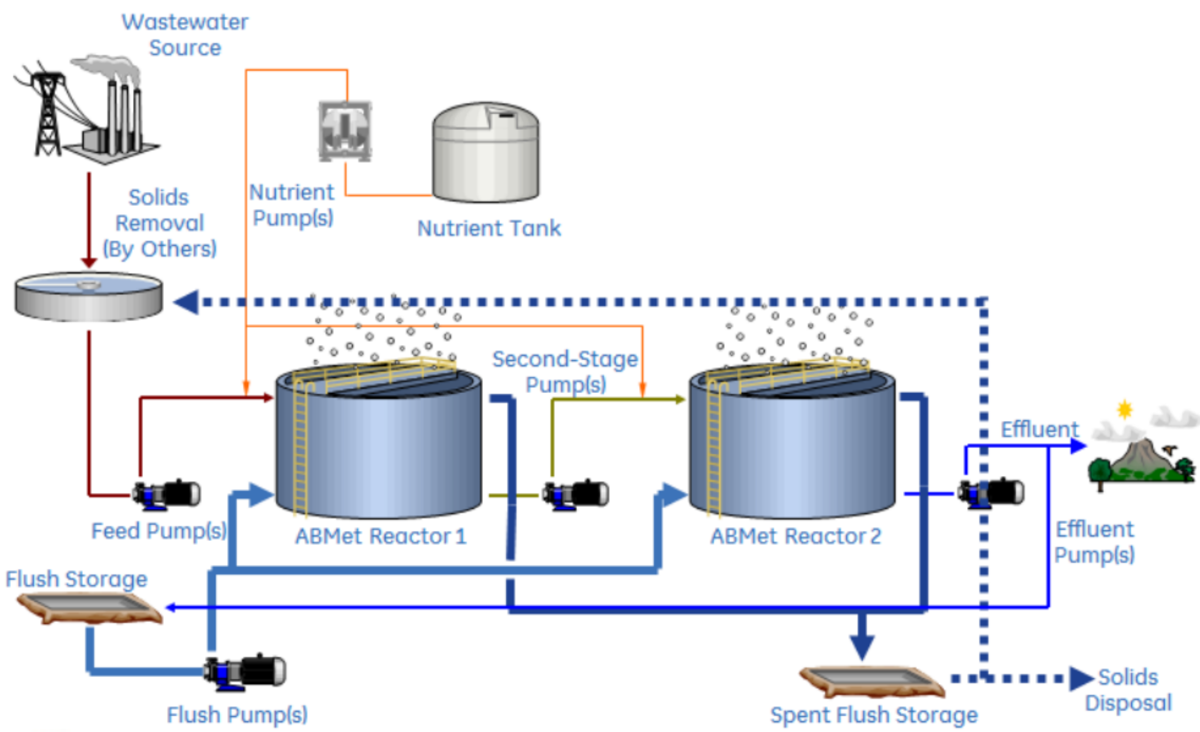

Figure 2: Process flow diagram of a two-stage ABMet system for biological selenium removal. ***Courtesy of Proceedings of the Water Environment Federation***

2.2 Metals removal from Bioreactor at Duke Energy

In 2009, the GE ABMet Bioreactor system went online at the Duke Energy facility. In the first year of operation, metal concentrations stayed relatively low and were reported in lbs/day. The middle of 2010 saw an upward shift in metals mainly in Selenium, Mercury, Boron, Thallium and Manganese. These metals exceeded NPDES permit limits as well as NC Surface Water Quality Standards as seen in Table 3.

In large quantities, these metals can be hazardous to the environment They are known to bioaccumulate in aquatic systems, settling out in sediment and then moving to the aquatic species (Hazrat et al., 2019). Table 3 and Figures 3 through Figure 7 show the increase of these metals over a 2-year period in 2010-2011 while the station was in bioreactor operation. Additional data showing the monthly average of metals as well as the annual average during the 2010-2011 period is included in Appendix A.

Metals	**2010-2011 Average ug/L**	**NPDES Permit/North Carolina Water Quality Standard Limits ug/L**
Selenium	14.18	5.0
Mercury	0.01	0.012
Boron	4742.66	750
Thallium	0.48	0.24
Manganese	146.79	200

Table 3: Se, Hg, B, Tl & Mn Levels in ug/L of Final Outfall in 2010-2011 at Duke Energy Facility. ***Courtesy of Duke Energy***

Selenium

Selenium concentration was very unstable throughout 2010 and 2011. It remained above the North Carolina Surface Quality limit of 5 ug/L throughout most of 2011. The highest concentration detected was in the month of February 2011. The issue with Selenium is that it can biomagnify through food chains in aquatic ecosystems receiving elevated Selenium inputs (Jasonsmith et.al, 2008). Selenium concentrations in food sources above 2–3 μg g−1 dry mass is considered to induce teratogenesis in fish spawning and deformities in fish larvae (Jasonsmith et. al, 2008).

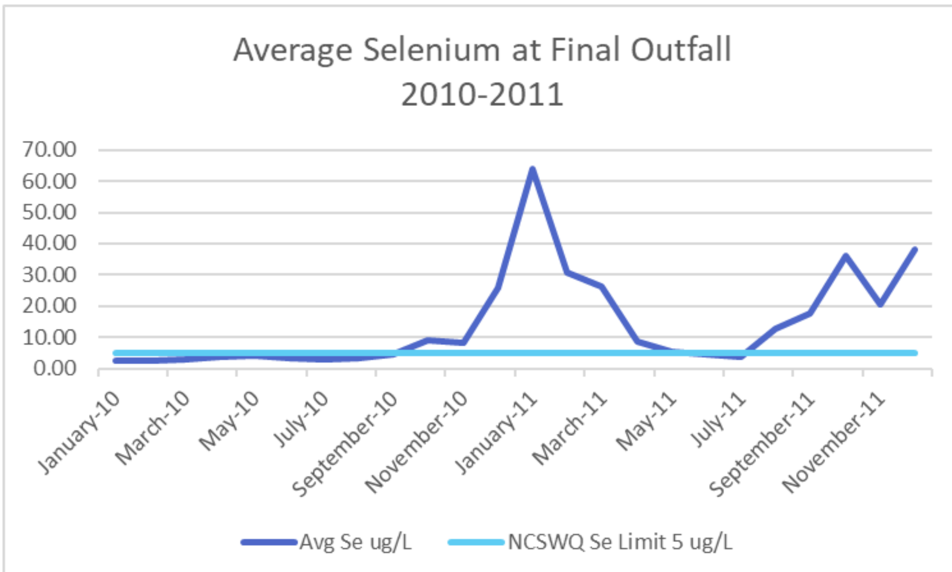

Figure 3: Annual Average 2010-2011 Se Levels in ug/L of Final Outfall compared to NC SWQ Standards at Duke Energy Facility. ***Courtesy of Duke Energy***

Mercury

Mercury concentration was also very unstable throughout 2010-2011. It remained above the limit of 0.012 ug/L throughout most of 2011. The highest levels of mercury were detected in February of 2011. Mercury also has a tendency to biomagnify up the food chain and can accumulate after large amounts are deposited. While Mercury is found naturally in the environment, high doses of organic compounds of Hg, particularly methylmercury, can be fatal to humans and wildlife, and even relatively low doses can seriously affect the nervous system of organisms. Mercury has also been linked to harmful effects on the cardiovascular, immune, and reproductive systems. Methylmercury passes through both the placenta and blood–brain barrier; therefore, the exposure of women of child-bearing age and of children to methylmercury is of great concern (Gworek et. al, 2020).

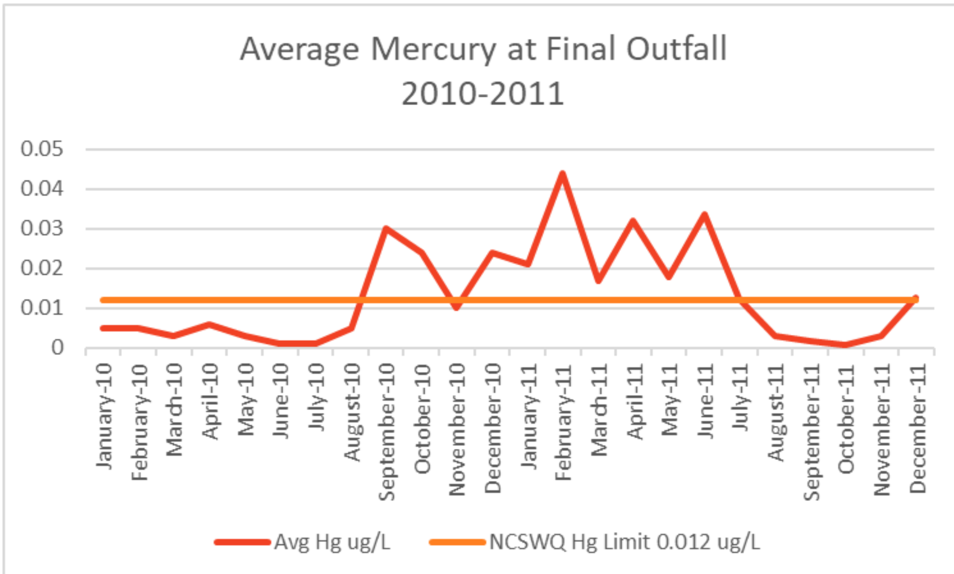

Figure 4: Annual Average 2010-2011 Hg Levels in ug/L of Final Outfall compared to NC SWQ Standards at Duke Energy Facility. ***Courtesy of Duke Energy***

Boron

Boron was unstable during 2010-2011 as well. It constantly remained substantially above the limit of 750 ug/L throughout this time. As with the previous constituents, the highest concentration was detected in February 2011. Boron is a naturally occurring metal in the environment. While most of the metals of concern at the Duke Energy facility can be lethal at concentrated doses, Boron is lethal at much higher doses. At prolonged exposure, Boron can be hazardous to the female reproductive system as well as fetuses (Eisler, 1990).

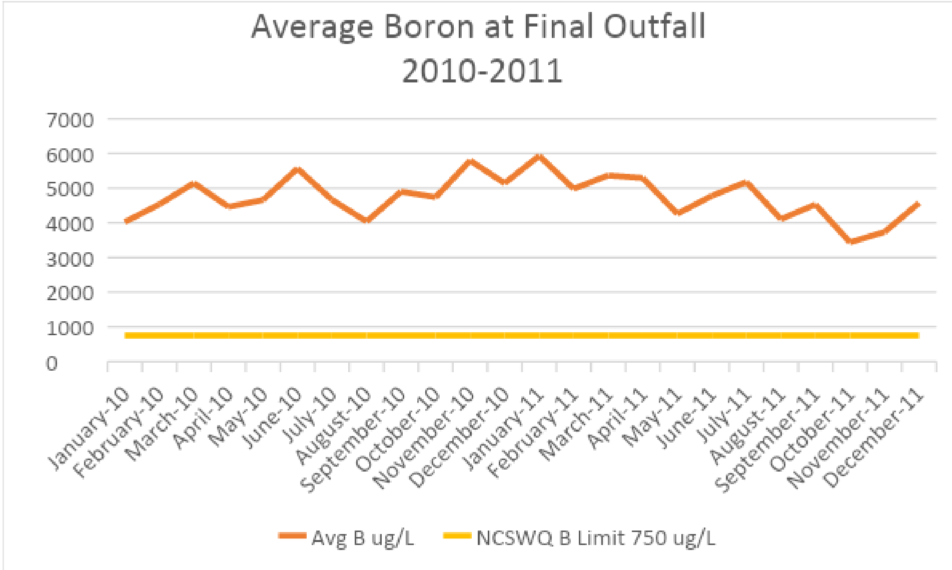

Figure 5: Annual Average 2010-2011 B Levels in ug/L of Final Outfall compared to NC SWQ Standards at Duke Energy Facility. ***Courtesy of Duke Energy***

Thallium

Thallium remained unstable during 2010-2011. There did, however, seem to be a downward trend of Thallium concentrations during the 2-year period but during that time most levels were above the 0.24 ug/L limit. The highest concentration was detected during January 2010. As with the other constituents, Thallium is found naturally in the environment as well but is seen with the combustion of fossil fuels. Thallium poisoning brings hair loss, gastroenteritis, polyneuropathy, fatigue, tiredness, headache, insomnia, nausea, and vomiting (Kazantzis, 2000).

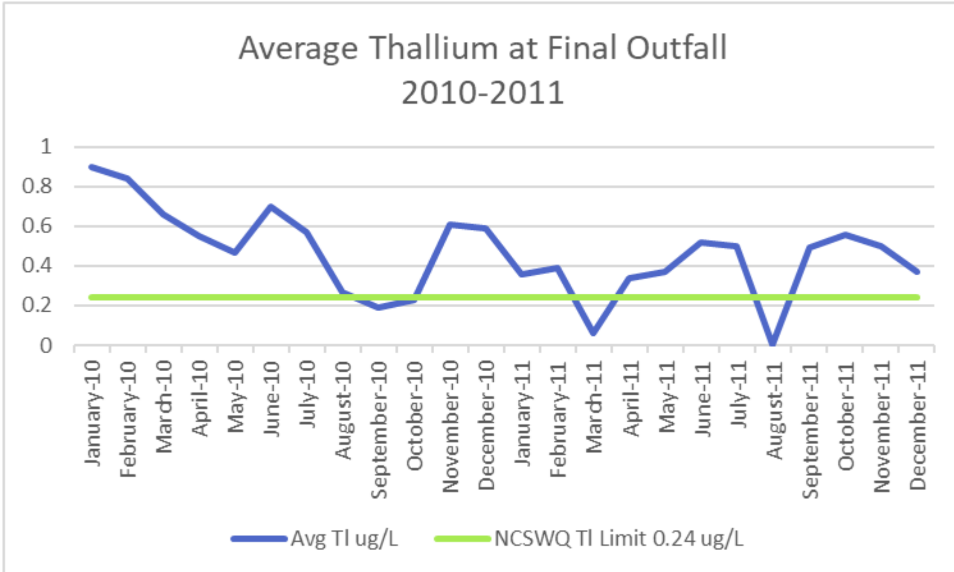

Figure 6: Annual Average 2010-2011 Tl Levels in ug/L of Final Outfall compared to NC SWQ Standards at Duke Energy Facility. ***Courtesy of Duke Energy***

Manganese

Manganese, like Thallium, remained unstable throughout 2010-2011. There were extended periods throughout these 2 years in which Manganese concentrations were below the limit of 200 ug/L, but spikes of the constituent can be seen as well. Manganese is a heavy metal that is found naturally in the environment. Although manganese is needed for our body, chronic exposure can yield many effects. In humans it can cause neurological, respiratory, reproductive, and developmental effects (Williams, 2012).

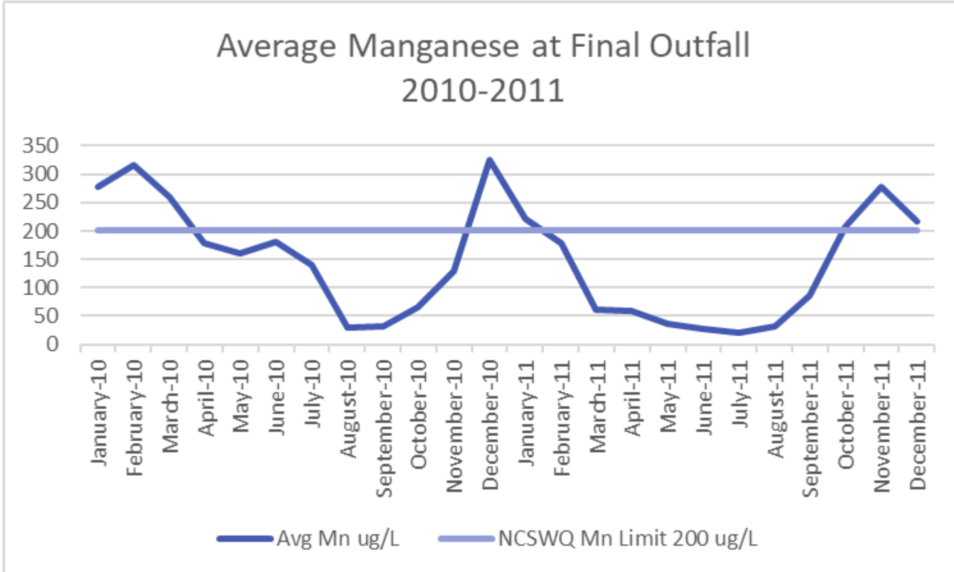

Figure 7: Annual Average 2010-2011 Mn Levels in ug/L of Final Outfall compared to NC SWQ Standards at Duke Energy Facility. ***Courtesy of Duke Energy***

Given the high levels of metals in the effluent water during this short amount of time and the low limits of the NPDES permit, a decision was made by the company in 2011 to conduct a FGD wastewater treatment study (Duke Energy, 2020). The following year, in 2012, the company then applied for a Special Order of Consent or SOC to the North Carolina Department of Natural Resources (NCDENR) now known as NC Department of Environmental Quality (NCDEQ). The limits of the SOC are described below in Table 4. This SOC required that the facility complete studies and evaluate wastewater technologies that would properly treat the FGD water from the coal-fired plant.

Metals	NCDEQ Issued SOC Limits for Final Outfall Daily lbs/day	NCDEQ Issued SOC Limits for Final Outfall Monthly lbs/day
Selenium	6.461	4.755
Mercury	0.0095	0.0037
Boron	683.0	590.7
Thallium	0.089	0.056
Manganese	29.4	22.1

Table 4: NCDEQ Issued SOC Daily & Monthly Limits for Se, Hg, B, Tl & Mn Levels in the Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energy***

2.3 Wastewater Treatment Study

The study that was initiated by Duke Energy was done to characterize wastewater discharges from the plant in preparation for expected operational and capital projects that will affect the wastewater discharges. Many technologies were considered for replacement to the Bioreactor, but the decision was made to implement the Zero Liquid Discharge (ZLD) technology on the FGD scrubber blowdown stream as well as implementation of dry bottom ash handling. A third-party company was hired to determine the wastewater discharge characterization and to estimate the ZLD inlet design chemistry, given the current and anticipated future regulatory environment and operational changes (URS Corporation, 2011). To accomplish this task, the following approach was taken to develop water balances for a series of operational scenarios, conduct reasonable potential analysis of discharge streams at the final outfall to the receiving stream to identify pollutants of concern under the scenarios, model the effects of the operational scenarios on the lake to estimate future lake characteristics and plant features, as well as calculate the estimated ZLD inlet design basis chemistry based on selected assumptions.

After different assumptions and scenarios were made, the basis for a wastewater management strategy at the Duke Energy facility, balances were developed for in-plant wastewaters, identifying the flow, mass loading and pollutant concentration of each stream under varying conditions. The wastewater streams considered for inclusion in the water balances include the FGD blowdown, ash sluice water, low volume waste, cooling tower blowdown and air heater wash water. At the time, FGD scrubber blowdown originated as overflow streams from the FGD gypsum dewatering system secondary hydrocyclones. These overflow streams were directed to holding tanks that were pumped to the gypsum settling pond. This wastewater stream had relatively low concentrations of non-dissolved (particulate) gypsum but contained dissolved gypsum at or above the solubility limits (i.e., it could be supersaturated). In addition, the FGD scrubber blowdown contains many pollutants, both dissolved and particulate. The bottom ash from the generating unit was sluiced to the ash settling pond where the ash was removed by clamshell equipment and set aside to dewater. The ash settling pond provided gravity settling. At the time of the study in 2011, no active process control was provided for the ash pond water. This has since changed with the current federal ash pond regulations. Under normal operations, fly ash is handled by a dry pneumatic system. However, during routine silo maintenance events, fly ash from all operational units was sluiced and sent to the ash pond. Station Low Volume Wastewaters include water flows from oily wastes, reject streams from various water treatment processes, and overflow from the water storage system. FGD blowdown was routed to the FGD Settling Pond for solids removal.

Historically, the pond discharge receives further treatment through the bioreactor before being discharged to the Ash Pond through an internal outfall.

Cooling tower blowdown was ultimately discharged to the Ash Pond then to the receiving stream through the final outfall. Of the total CTBD stream, a third was discharged via internal outfall to serve as the water source for ash sluicing. The ash sluice stream was typically just bottom ash sluice and then discharged into the ash pond where the entire water flow was assumed to make it to the final outfall, less some contaminant removal across the pond. The remaining CTBD water bypassed the internal outfall and directly entered the ash pond. Wash water from the air heaters was discharged to the ash pond as well. Although discharge of air heater water occured for approximately 16 to 36 hours twice a year, this stream could contribute significant loads of selected analytes, such as TDS, aluminum, and calcium, along with low pH to the ash pond.

To determine pollutants of concern in the wastewater streams described above, pollutant concentrations at the outfall locations, as determined from the plant water balance, were compared with current and projected water quality standards. As the Duke Energy plant discharges into the receiving stream, no dilution factor for the receiving stream has been allowed by regulatory agencies, and thus was not used in the study. Additionally, because the mass balance data were based on a limited number of samples, a true reasonable potential analysis would likely overstate the pollutants of concern due to the large ‘measure of safety’ factor that would be applied to each pollutant correlating to uncertainty. Thus, the estimated concentrations at the outfall from the mass balance were compared directly with the water quality standards. It is important to note that the mass balance data are based on analyses of a limited number of sampling events, and hence, there is resulting uncertainty in the identified pollutants of concern from the analysis.

In the conclusion of the wastewater study, many different scenarios were considered for the design of the future ZLD system. The scenarios were predicted to span over a ten-year period and out of those cases, all managed to show a decrease of the five constituents of concern, Se, Hg, B, Tl & Mn. During the three case scenarios, all five constituent cases had predicted concentrations well below the facility's NPDES permit limit as shown in Figures 8 through Figure 12. As the study was conducted to prove, the ZLD technology was chosen to replace the bioreactor to treat the FGD wastewater of the Duke Energy Facility.

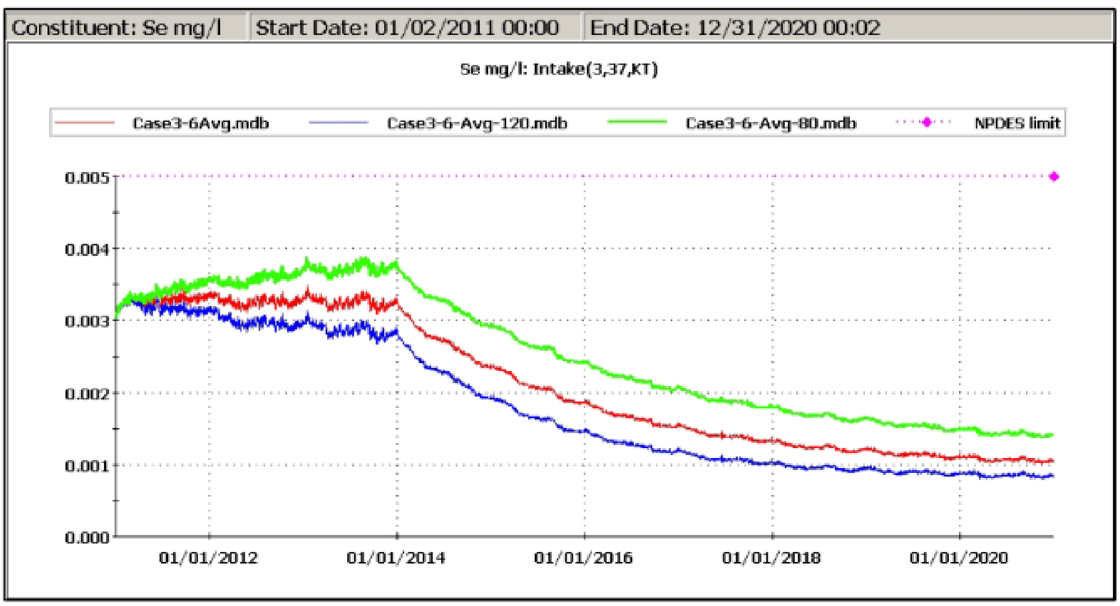

Figure 8: Time Series Plots of Se Water Quality Concentrations Compared to Potential Water Quality Limit in Receiving Streams. ***Courtesy URS Corporation***

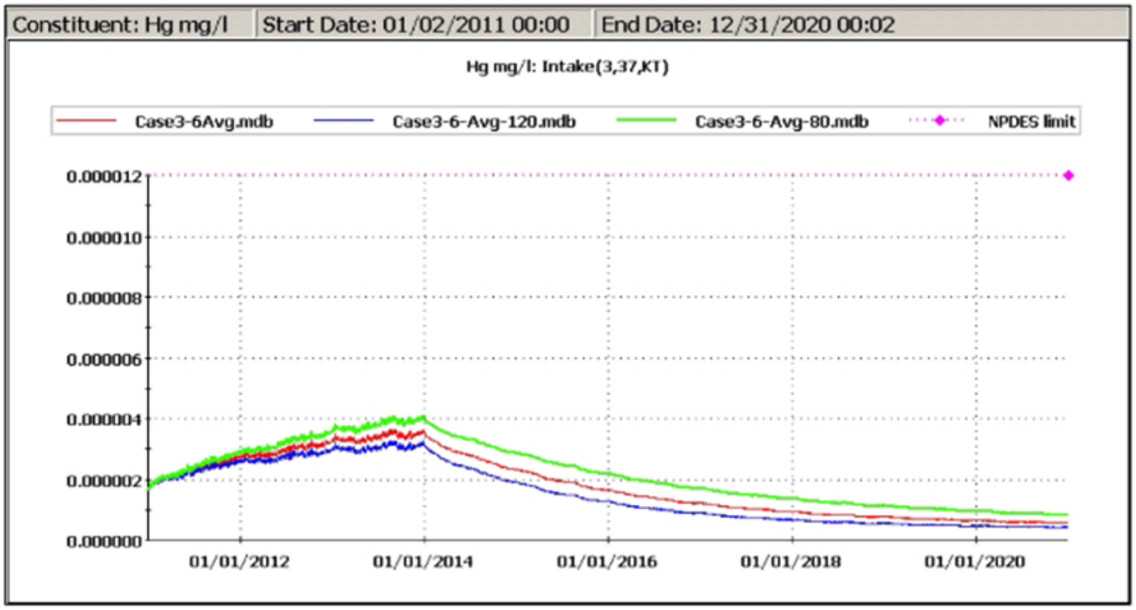

Figure 9: Time Series Plots of Hg Water Quality Concentrations Compared to Potential Water Quality Limit in Receiving Stream. ***Courtesy URS Corporation***

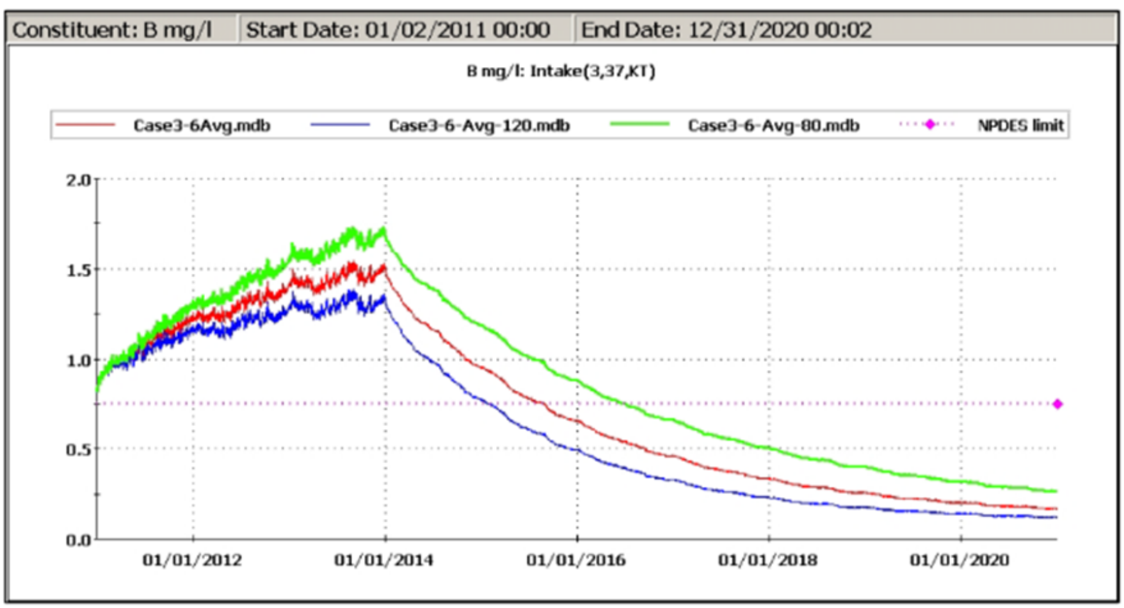

Figure 10: Time Series Plots of B Water Quality Concentrations Compared to Potential Water Quality Limit in Receiving Streams. ***Courtesy URS Corporation***

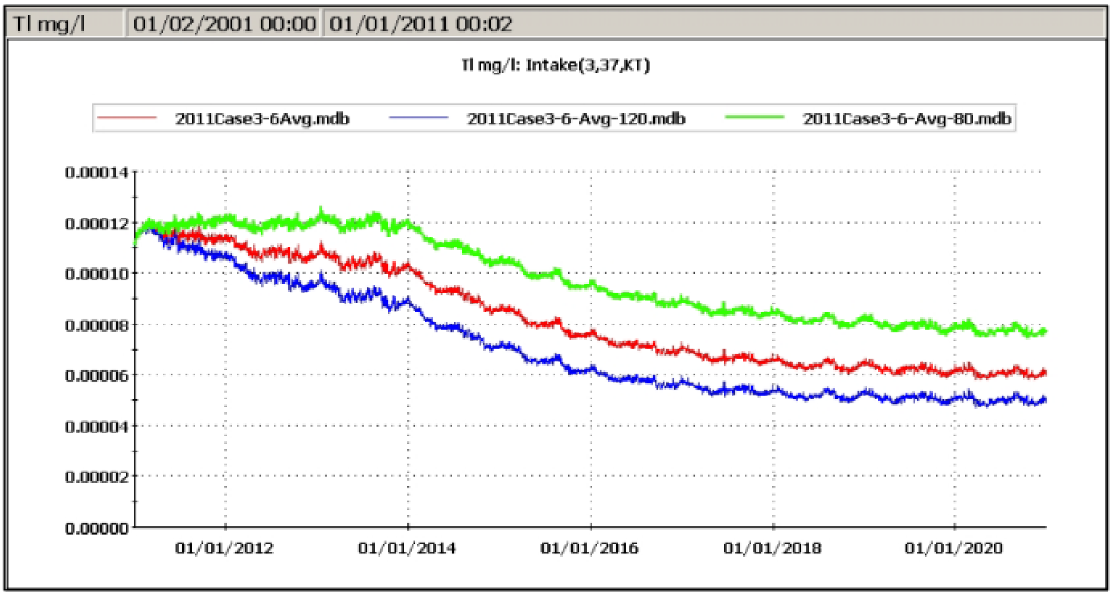

Figure 11: Time Series Plots of Tl Water Quality Concentrations Compared to Potential Water Quality Limit in Receiving Stream. ***Courtesy URS Corporation***

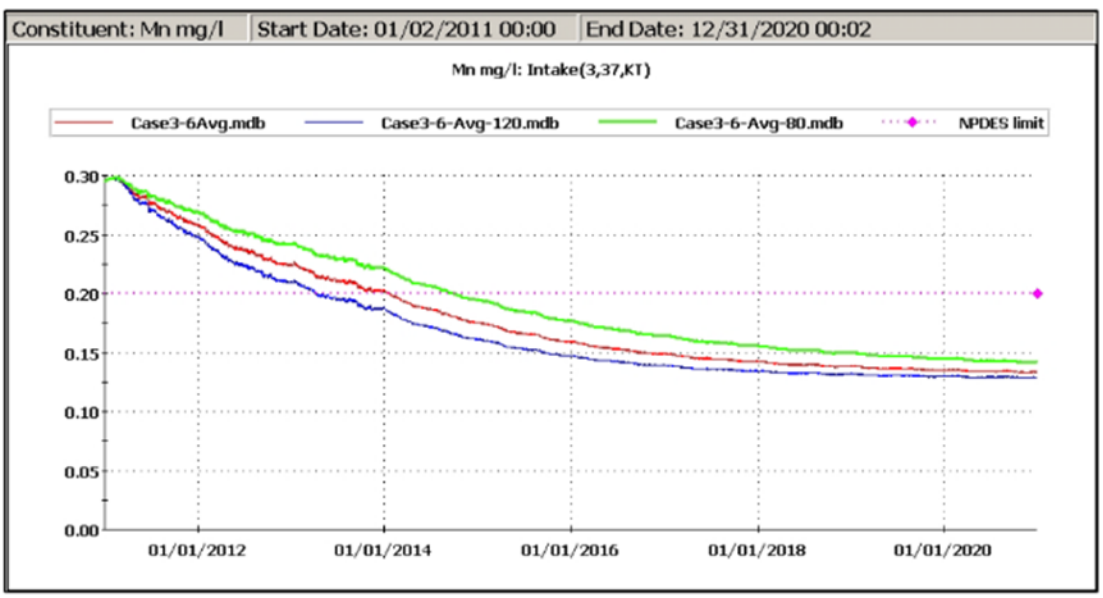

Figure 12: Time Series Plots of Mn Water Quality Concentrations Compared to Potential Water Quality Limit in Receiving Stream. ***Courtesy URS Corporation***

3. Zero Liquid Discharge Technology Replacement at Duke Energy

As the 3rd party wastewater study concluded, the best technology that was selected was the Zero Liquid Discharge (ZLD) or Thermal Evaporator process. With the partial ZLD option, the resulting brine was used for fly ash wetting and disposal in the onsite landfill. Because fly ash is sometimes sold, further consideration was given for evaporation and complete crystallization, thereby avoiding the dependence of brine disposal on ash disposal. In all options, the settling pond was continued to be utilized for gypsum solids settling, the bioreactor treatment system was removed from service, and effluent from the settling pond was fed to the ZLD system. Construction for the ZLD at Duke Energy began in October 2012 and went online in December 2013 (Duke, 2020).

3.1 ZLD Technology

The most important parameter in evaluating ZLD technologies is chloride concentration. Chloride mass flow rates are determined by the chloride content of the coal burned, and the flow rate of the FGD blowdown is adjusted to maintain the maximum chloride concentration allowable by the FGD metallurgy. The Duke Energy facility prior to ZLD operation, operated at a chloride concentration of around 6,000 mg/L. The current scrubber materials of construction allow operating at a concentration of up to 10,000 mg/L, but the metallurgy of the absorber could be modified to allow a chloride concentration of 20,000 mg/L, reducing the flow of blowdown.

For eliminating the discharge of FGD wastewater to the Duke Energy receiving waterbody, a partial ZLD was constructed where all the residual brine is used for fly ash conditioning prior to disposal in a landfill indicated in Figure 13. The volume of wastewater is reduced by evaporation to a low (18 to 24 gpm) flow. This option requires that all or most of the fly ash be dedicated to water disposal, limiting potential fly ash sale.

At the Duke Energy fossil fueled plant, the partial ZLD consists of falling film evaporator (Primary Evaporator) for a total of 370 GPM as well as forced circulation evaporator (Secondary Evaporator) to concentrate up FGD blowdown into a concentrated brine and distillate stream. The following Brine Cooler decreases the brine temperature prior to storage. Concentrated brine mixed with fly ash is disposed of at an on-site landfill while the distillate water is used throughout the plant, reducing water make-up (Loewenberg, 2013).

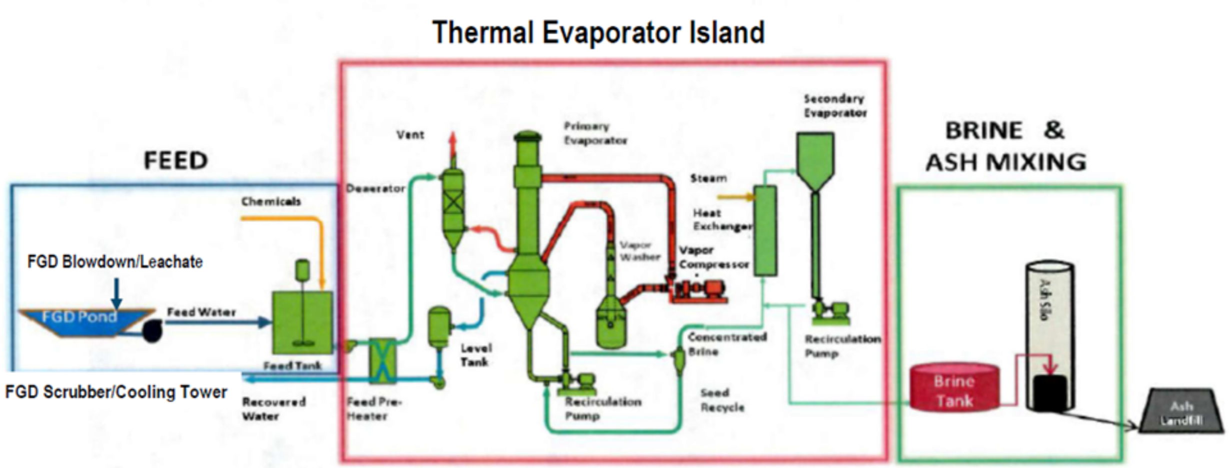

Figure 13: ZLD System at Fossil-Fuel Electric Generating station. ***Courtesy of GEA Process Engineering***

3.2 Primary Evaporator

There are 3 Primary Evaporator trains that are used for much of the concentration. It is a falling film type evaporator with a mechanical vapor compression system outlined in Figure

14. Given the nature of the FGD blowdown, the system is operated as a seed system. The FGD wastewater is introduced into one of two 100% plate heat exchangers per PE to preheat the wastewater against the hot distillate from the falling film evaporator. The preheated wastewater is additionally heated by the vent stream from the falling film evaporator shell side to further optimize the energy consumption of the system. This preheating takes place in a two-stage flash system called a deaerator.

The wastewater subsequently enters the sump of the falling film evaporator. Here the recirculation pump transfers the liquid to the top tube sheet where the wastewater enters the heat transfer tubes, creating a thin film of cascading water. In a seed evaporation system, the predominate crystal (seed) in the system is used and artificially introduced into the feed stream. The seed crystals act as nucleation sites for the subsequent calcium sulfate precipitate and crystal growth as the FGD blowdown is concentrated.

The seeding process is self-sustaining and after an initial seeding, further seed addition is not required. To recover the seed crystals from the concentrated solution, a hydrocyclone is utilized where the overflow is sent to the Secondary Evaporator Feed Tank and the underflow, seed rich fraction, is collected in a Seed Slurry Tank, and later combined with the un-concentrated FGD blowdown.

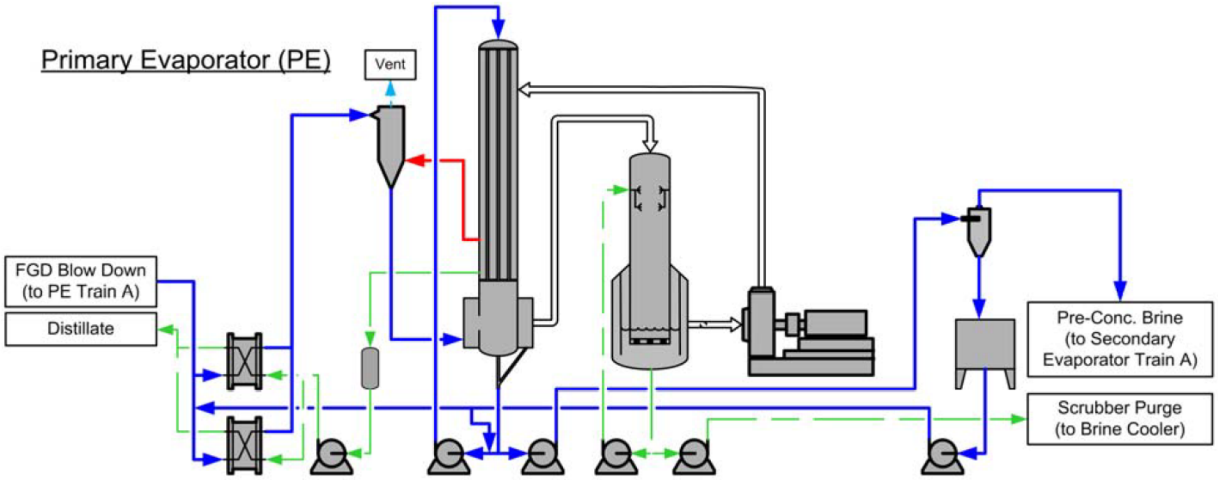

Figure 14: One of Three Primary Evaporator, Falling Film Type Evaporator with Mechanical Vapor Compression. ***Courtesy of GEA Process Engineering***

3.3 Secondary Evaporator

The concentrated FGD blowdown from the three Primary Evaporator trains will be further concentrated in one of the two Secondary Evaporators shown in Figure 15, since the primary evaporation step is limited to concentrate the wastewater close to the saturation point of the main salts in the solution, sodium chloride and calcium chloride. For the remaining concentration, a successive evaporation step is required to reduce the wastewater volume to match the available fly ash for mixing. The concentrated wastewater is introduced into the recirculation loop where the temperature is increased in a shell and tube heat exchanger that is heated with plant steam. Boiling in the heat exchanger is suppressed by its elevated pressure. The generated water vapor is subsequently condensed in a shell and tube condenser and combined with the Primary Evaporator distillate for use within the plant.

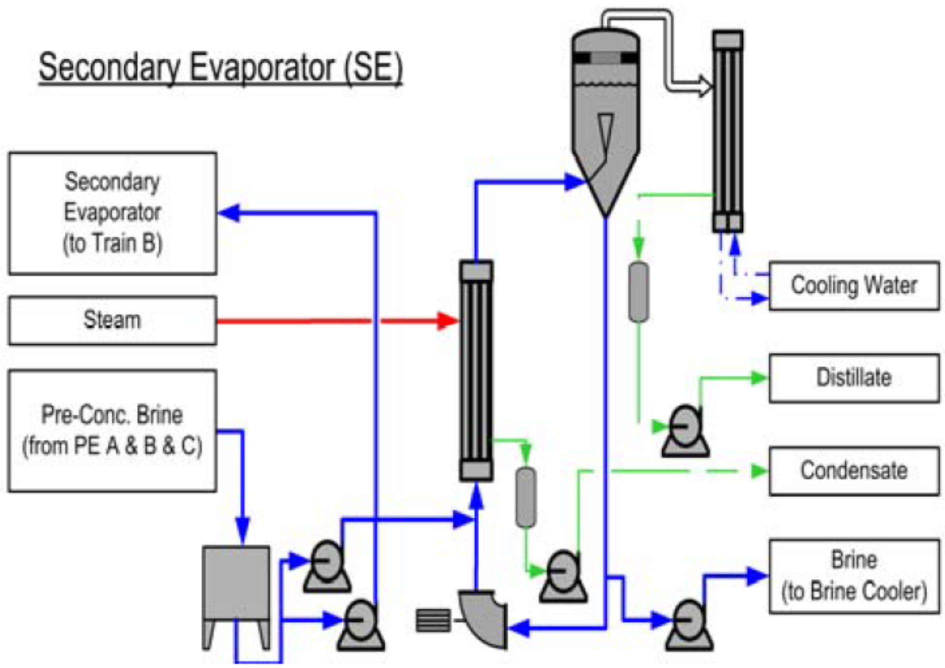

Figure 15: One of Two Secondary Evaporator, Forced Circulation Type Evaporator.

Courtesy of GEA Process Engineering

3.4 Brine Cooler and Fly Ash Mixing

Prior to storage of the concentrated wastewater (Brine) in the Brine Tanks, the solution is cooled in a Brine Cooler displayed in Figure 16. The solution is cooled to approximately 140°F, which allows the use of less expensive FRP. The brine is continuously pumped to the two fly ash silos in one of two brine piping recirculation loops (highways). Each brine loop can feed each of two new fly ash mixers. The fly ash and brine mixture are loaded into dump trucks and hauled to an on-site lined ash storage landfill with a leachate collection and use system.

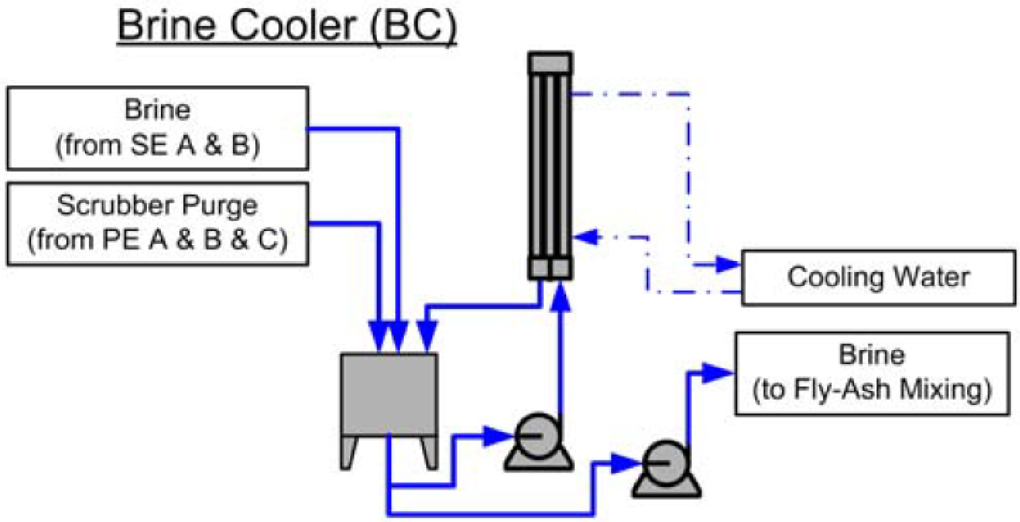

Figure 16: One of Two Brine Coolers, Recirculated Type Cooler. ***Courtesy of GEA Process Engineering***

4. Success of Zero Liquid Discharge at Duke Energy

The installation of the Zero-Liquid Discharge system at the Duke Energy coal-fired plant is the culmination of site-specific situation and constraints, and development of alternative FGD wastewater treatment methods. The capability to remove multiple constituents from the FGD blowdown and recover high quality distillate made this the solution of choice for the unique conditions at the plant.

With the introduction of the ZLD in late 2013/early 2014, there has been a shift in the concentration of the metals of concern (Se, Hg, B, Tl & Mn). This steady decrease was seen in the monthly discharge monitoring reports (DMR) as well as the annual Biological Monitoring Report that Duke Energy is responsible for submitting to NCDEQ. The areas of focus that are outlined in these reports are the water quality/chemistry of the final outfall to the receiving body, sediment, and aquatic life of the receiving body. For the purposes of this review, we will focus on the final outfall from the Duke Energy facility and the transects in the receiving body that are downstream from the outfall as seen in Figure 17.

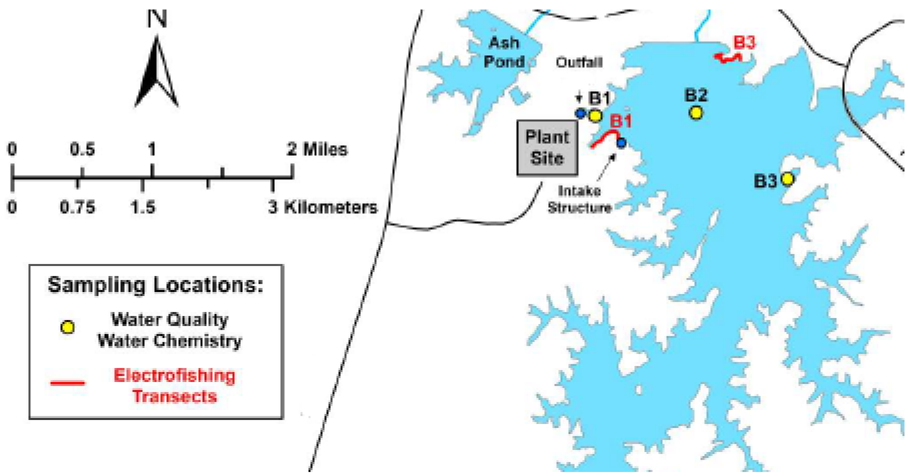

Figure 17: Final Outfall and Receiving Water Body Transect Sample Locations. ***Courtesy of Duke Energy Natural Resources Department***

4.1 Improved Metals Removal from Effluent by ZLD

In reviewing the 2015 monthly Discharge Monitoring Reports (DMR) from the Duke Energy facility, a significant decrease in concentrations was noted. Table 5 shows the annual average of each metal in 2010-2011 after a year of service from the bioreactor compared to the annual average in 2015 after about a year of service from the ZLD. The change in Selenium was 94.81%, Mercury was 93.21 %, Boron was 64.88 %, Thallium was 50.43% and Manganese was 68.79%. Constituent concentrations have continued to decrease or remain constant in the last 8 years since the ZLD went into service. The concentration of the metals of concern as compared to the NCSWQ standards are displayed in Figures 18-22 for the year 2015.

The NCDEQ-issued SOC was maintained from 2012 until 2017 when the Final Written Account was submitted to the Raleigh Regional office. The change of operation from bioreactor to ZLD caused the reduction in constituents and all were maintained well below the permit limits of the NPDES SOC. The Duke Energy fossil fuel plant maintained compliance during these years of operation and will continue to do so through 2022. During these years of elevated metals, ecological conditions in the receiving reservoir have been minimal. When the FGD operation commenced in 2009, there were no biologically detrimental effects that were observed.

Metals	2010-2011 Average ug/L	2015 Average ug/L	Percent Change
Selenium	14.18	0.74	-94.81
Mercury	0.01	0.0008	-93.21
Boron	4742.66	1665.56	-64.88
Thallium	0.48	0.23	-50.43
Manganese	146.79	45.81	-68.79

Table 5: Annual Average of Se, Hg, B, Tl & Mn concentrations at Final Outfall in 2010-2011 compared to 2015 Averages and Percent of Change. ***Courtesy of Duke Energy***

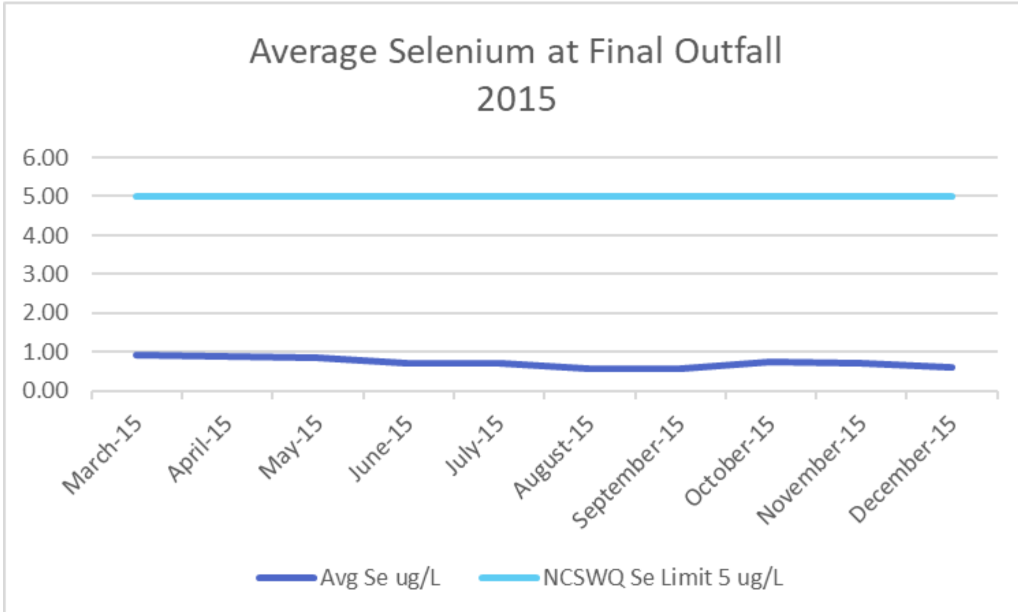

Figure 18: Annual Average 2015 Se Levels in ug/L of Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energy***

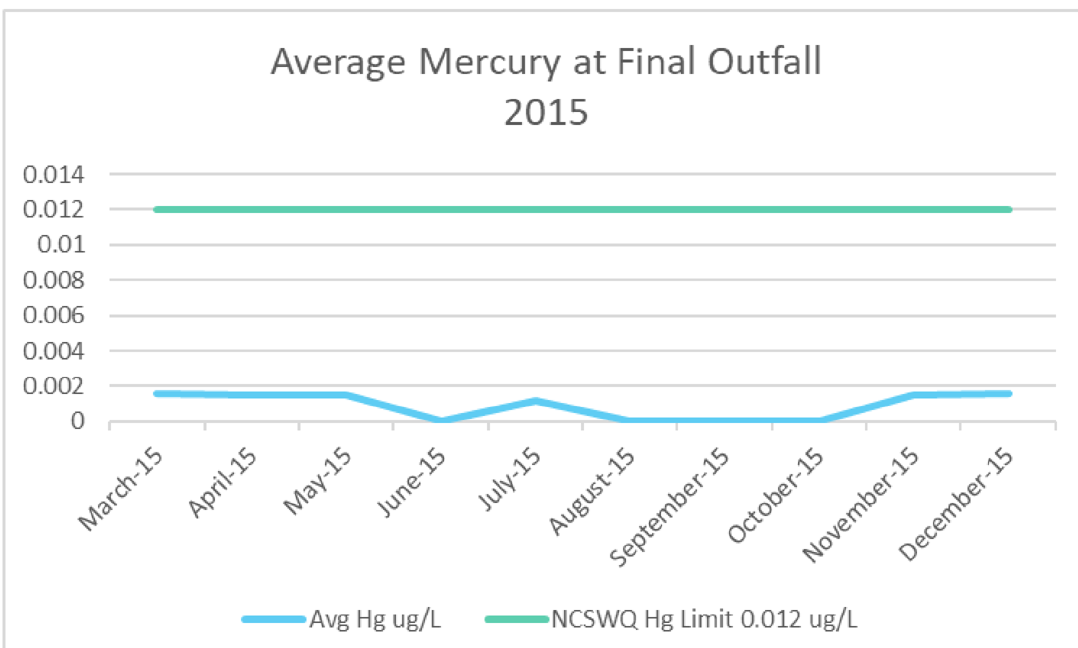

Figure 19: Annual Average 2015 Hg Levels in ug/L of Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energy***

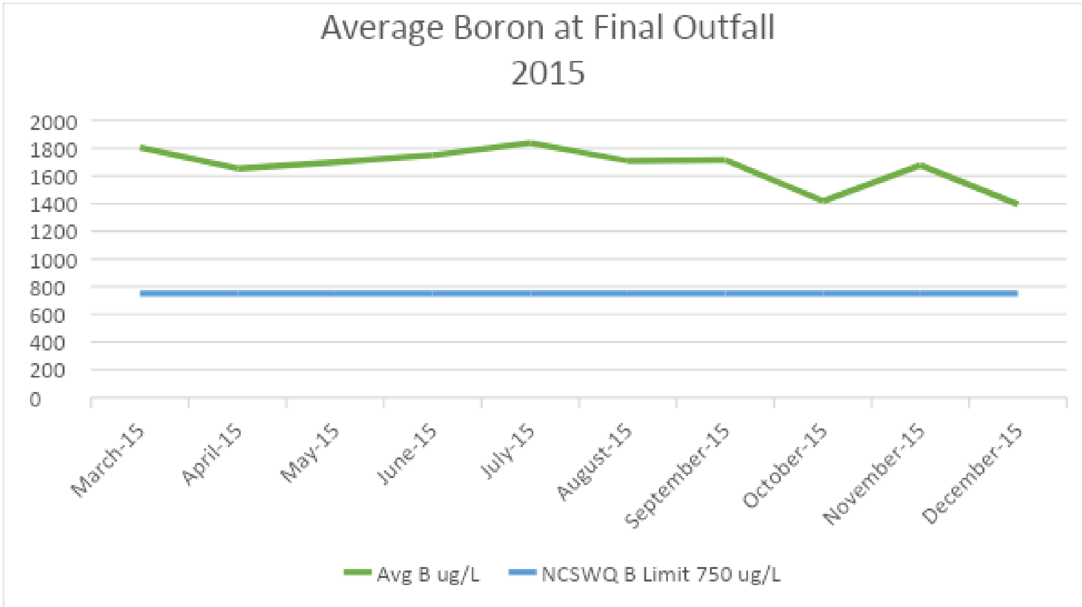

Figure 20: Annual Average 2015 B Levels in ug/L of Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energy***

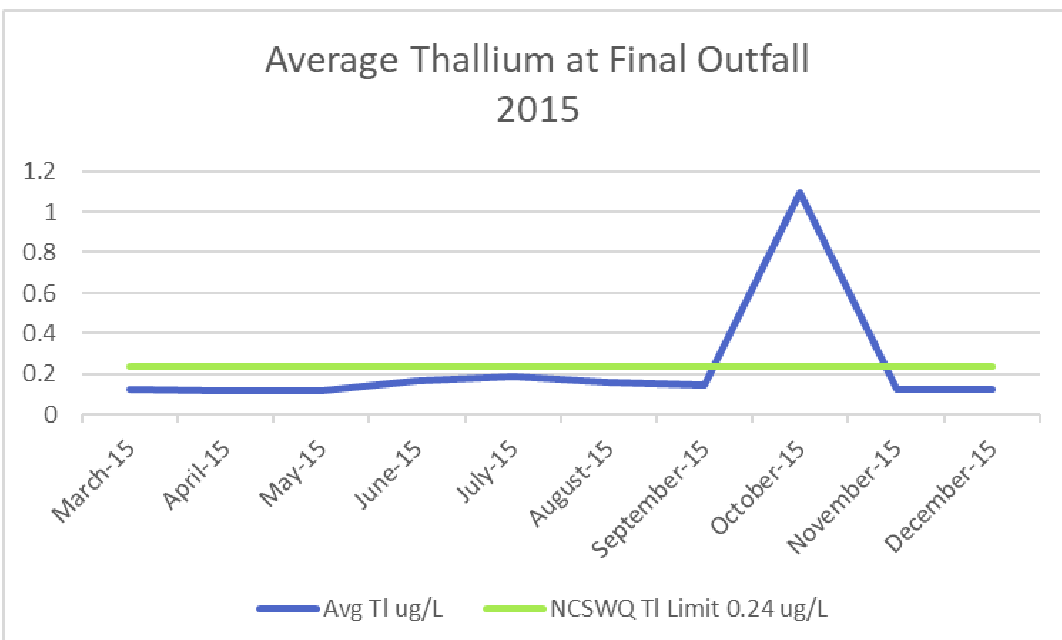

Figure 21: Annual Average 2015 Tl Levels in ug/L of Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energy***

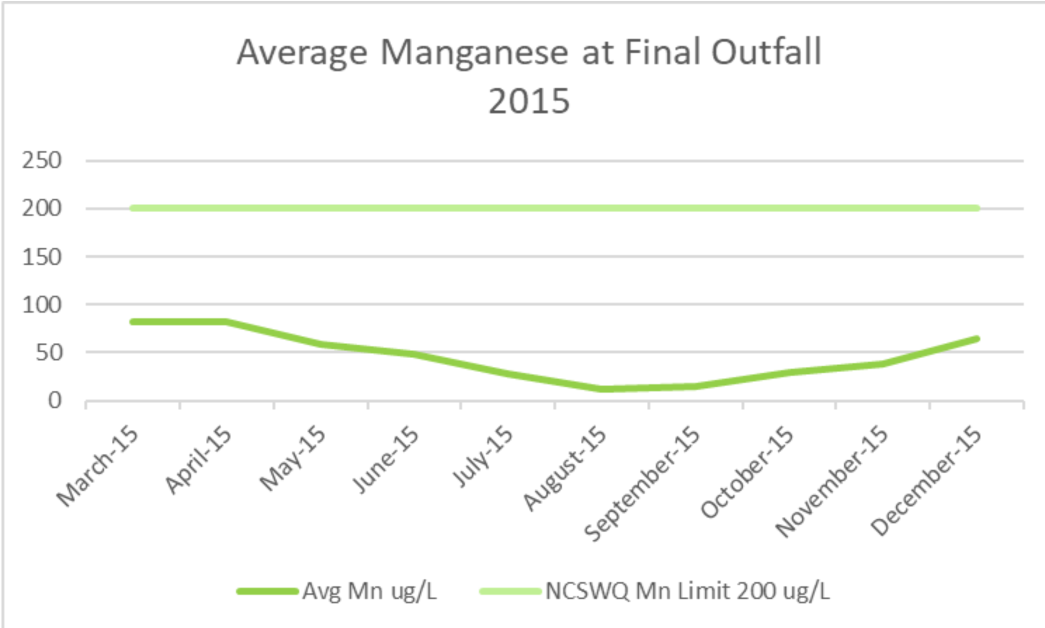

Figure 22: Annual Average 2015 Tl Levels in ug/L of Final Outfall at Duke Energy Facility. ***Courtesy of Duke Energ***

4.2 Improvements in Water Quality/Chemistry in Receiving Reservoir

As expected in the reservoir, improvements to ecological conditions were seen in the 2015 Biological Monitoring report submitted to NCDEQ by Duke Energy. At this point the ZLD had been in service for a year and the concentrations of metals had continued to decrease or remain steady and have been since. The receiving reservoir has a relatively small watershed area, low water inflow and limited shoreline development. It is also a relatively small lake compared to ones in the nearby area. This makes for any increase in metals, detrimental to the ecosystem. As seen in Figure 17 of the sample locations, the concentration of the metals was the greatest at Station B1 near the ash basin discharge but were still low and were less than the North Carolina Water Quality Standards.

Selenium was the only metal that had biomagnified the food chain but remained in low quantities in fish tissue. As expected, the greatest amount of bioaccumulated selenium was seen at the immediate vicinity of the ash basin discharge. Although elevated, these concentrations were still below those seen in 2012, 2013 and 2014. Selenium has continued to be on the decline and will be in current 2022. Figure 23 showcases the decrease in Selenium concentration within the reservoir. With the commencement of ash basin closure to the facility and dewatering of the ash basin, there is a potential for change in water quality if adequate treatment is not met.

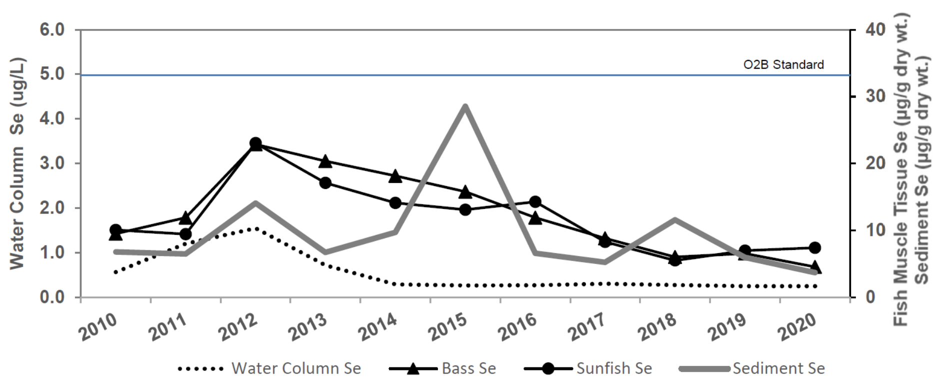

Figure 23: Annual Mean Water Column, Fish Tissue and Sediment Selenium Concentrations at Transect B in Receiving Reservoir, 2010-2020. ***Courtesy of Duke Energy***

4.3 ZLD Usage in the United States and Challenges

Currently, most ZLD systems in the world are operational in the USA. Initial development of ZLD dates to the 1970s when power plants near the Colorado River adopted ZLD systems due to the increasing salinity of river water (Yaqub, 2019). Today, ZLD is mainly applied in the power generation sector to treat and recycle the FGD wastewater and cooling tower blowdown. A survey of operational ZLD systems in 2008 showed that around 60 out of 82

ZLD plants were associated with the power industry while the rest were used in various industries including chemical, mining, electronics, nuclear, and fertilizer industries (Yaqub, 2019). Compliance with newly introduced standards for wastewater discharge provides incentives for ZLD installations at power plants. In North USA, it is forecast that the ZLD market will increase by $109.8 million between 2017 and 2025, reaching $243.9 million. These systems have potential for success for the power industry as well as oil & gas, chemical, petrochemicals, mining and other industries that generate large volumes of wastewater that must be managed (Aquatech, 2017).

Treatment of coal-fired power plant wastewater is becoming more complicated. With requirements to reduce acid-rain-causing emissions, plants have installed high efficiency FGD equipment. This equipment produces wastewater that contains high concentrations of dissolved salts—predominately chloride, calcium, and magnesium—but also concentrations of toxic constituents such as mercury, selenium, arsenic, and boron. Each of these contaminants has been regulated, with increasingly more stringent limits being enforced. Specialized treatment processes have been developed for individual constituents, resulting in increasingly complicated wastewater treatment schemes being required to meet permitted limits. With limits being imposed that stretch the effectiveness of known treatment technologies, ZLD treatment becomes a more viable solution. In addition, if constituents such as chlorides and other dissolved solids require removal, ZLD becomes the default option to concurrently meet discharge limits.

The ZLD does come with challenges, however. It can be costly to maintain and does require continued maintenance to operate properly. There is also the issue of water balance and in recent years the greater need of renewables and decreased dispatch of coal fired units makes it more difficult to produce ash to mix with the brine for disposal. In these situations, the brine solution is hauled off-site by a 3rd party vendor for treatment, which incurs a high cost.

5. Conclusion

The treatment of industrial wastewater has been a challenge in the 20th and 21st centuries. Planning and development for different technologies is essential for pollutant removal in the wastewater before discharge to receiving water bodies. Given the state and federal air regulation requirements and the initiation of the FGD system in 2009, the Duke Energy coal-fired plant met some challenges meeting NPDES permit limits. The technology of the time was adequate when the FGD went into service but eventually became non-compliant by exceeding NPDES limits given to the station by NCDEQ. Pollutants in the FGD wastewater which exceeded limits were Selenium, Mercury, Boron, Thallium and Manganese. After increased concentrations, a decision was made to conduct a wastewater study of the facility in 2011 as well as apply for a Special Order of Consent from NCDEQ in 2012.

At the conclusion of the wastewater study, the Zero Liquid Discharge (ZLD) technology was selected as the best alternative to treat the Duke Energy facility's wastewater. The implementation of the ZLD system is considered a significant strategy for industrial wastewater management and can diminish water contamination as well as enhance water supplies (Yaqub, 2019). With the introduction to the ZLD system in late 2013/early 2014, the water quality and water chemistry at the final outfall of the plant as well as the reservoir improved significantly. With a decrease of the metals of concern which were Selenium at 94.81%, Mercury at 93.21%, Boron at 64.88%, Thallium at 50.43 % and Manganese at 68.79% in 2015, the technology seems to be operating per design and efficient in pollutant removal.

The installation of the ZLD has come with technical challenges in the last 8 years. High capital costs and high energy usage can be encountered with daily use (Xiong, 2017). Maintenance is essential for the operation of the ZLD and must be periodically conducted to maintain efficiency. This has posed a challenge for the Duke Energy facility to allocate enough funds to properly service the system. Another challenge that the plant faces is reduced run times and in return, fly ash not being produced. Without the production of fly ash, the brine is unable to mix and be disposed of in the onsite landfill. Another cost is accrued for disposal of the brine mixture to an offsite 3rd party waste vendor.

For use in industrial settings, the ZLD technology has become essential for eliminating pollutants from FGD wastewaters. As this study has shown, the removal of metals from the wastewater effluent and increasing water reuse are the main responsibilities of the ZLD system. Within the last decade, there has been a shift towards an increase to renewable energies and these energies compete with coal fire generation. As no new coal facilities will likely be built in the future by Duke Energy or other energy companies within the US, existing fossil fuel plants with FGD systems can utilize this technology for metals removal. Further studies would be needed to analyze the ZLD technology for cost benefit and appropriate application for other wastewater treatment.

6. References

Ali, H., Khan, E., & Ilahi, I. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*, 1-15.

Aquatech. Zero Liquid Discharge. (2017). Retrieved April 2022 from https://www.aquatech.com/solutions/zero-liquid-discharge/

Citulski, J., Goel, R., & Snowling, S. (2016). Optimization of ABMet Biological Selenium Removal through Advanced Process Modelling. *Proceedings of the Water Environment Federation*. 949-961.

Duke Energy Progress, LLC, Raleigh, NC. (2010, 2011, 2015) Monthly Discharge Monitoring Reports

Duke Energy Progress, LLC, Raleigh, NC. (2012) Duke Energy Plant 2011 annual environmental monitoring report.

Duke Energy Progress, LLC, Raleigh, NC. (2016) Duke Energy Plant 2015 annual environmental monitoring report.

Duke Energy Progress, LLC, Raleigh, NC. Powerpoint Presentation, (2020). Dry Bottom Ash and FGD WWT.

Duke Energy Progress, LLC, Raleigh, NC. (2021) Duke Energy Plant 2020 annual environmental monitoring report.

Eisler, R. (1990). Boron Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. *U.S. Fish and Wildlife Service Biological Report: Contaminant Hazard Reviews.* 1-39.

Gworek, B., Dmuchowski, W., & Baczewska-Dabrowska, A.H. (2020). Mercury in the terrestrial environment: a review. *Environmental Science Europe*. 1-19.

Jasonsmith, J.F., Maher, W., Roach, A.C., & Krikowa, F. (2008). Selenium bioaccumulation and biomagnification in Lake Wallace, New South Wales, Australia. *Marine and Freshwater Research*, 1048-1060.

Kazantzis, G. (2000). Thallium in the Environment and Health Effects. *Environmental Geochemistry and Health*. 275-280

Loewenberg, M., Johnson, D., & Edelen, J. (2012). Zero-Liquid Discharge System at Duke Energy. 1-10.

Mohammadi, S., Ahmadi, M. H., & Ehsani, R. (2021). Optimization of combined Reverse Osmosis: thermal Zero Liquid. *Journal of Thermal Analysis and Calorimetry*, 1863-1871

North Carolina Department of Environmental Quality. Clean Smokestacks Act. (2022). Retrieved April 2022 from https://deq.nc.gov/about/divisions/air-quality/air-quality-outreach/news/clean-air-legislation/clean-smokestacks-act

North Carolina Department of Environmental Quality. North Carolina Water Quality Standards Table. (2021). Retrieved March 2022 from https://deq.nc.gov/ncstdstable07262021

Power Magazine. Advanced Process Control for Optimizing Flue Gas Desulfurization. (2018). Retrieved March 2022 from https://www.powermag.com/advanced-process-control-for-optimizing-flue-gas-desulfurization/

United States Environmental Protection Agency. Air Pollution Control Technology Fact Sheet, (2003). Retrieved March 2022 from http://www.epa.gov/ttn/catc/dir1/ffdg.pdf

United States Environmental Protection Agency. 40 CFR Parts 50, 53, and 58. (2009). Retrieved March 2022, from https://www.govinfo.gov/content/pkg/FR-2009-12-08/pdf/E9-28058.pdf

URS Corporation. (2011). Wastewater Characterization Study.

Water Technology. An Overview of Coal-Fired Power Plant FGD Wastewater Treatment - Coal Combustion and Emissions Control. (2006). Retrieved March 2022 from https://www.watertechonline.com/home/article/14171806/an-overview-of-coalfired- power-plant-fgd-wastewater-treatment-coal-combustion-and-emissions-control

Williams, M., Todd, G.D., Roney, N., Crawford, J., Coles, C., McClure, P., Garey, J., Zaccaria, K., & Citra, M. (2012). *Toxicological Profile for Manganese. Atlanta (GA): Agency for Toxic Substances and Disease Registry (US),* 1-556.

Xiong, R., & Wei, C. (2017). Current status and technology trends of zero liquid discharge at coal. *Journal of Water Process Engineering*, 346-351.

Yaqub, M., & Lee, W. (2019). Zero-liquid discharge (ZLD) technology for resource recovery from. *Science of Total Environment*, 551-563.

7. Appendices

Month/Year	Selenium	Mercury	Boron	Thallium	Manganese
Jan. 2010	2.52	0.005	4023.5	0.9	278.5
Feb. 2010	2.40	0.005	4532.5	0.84	316.8
Mar. 2010	2.87	0.003	5146	0.66	258.6
Apr. 2010	3.72	0.006	4460	0.55	177.5
May 2010	3.96	0.003	4657.5	0.47	159.5
Jun. 2010	3.35	0.001	5564	0.7	181
Jul. 2010	2.95	0.001	4662.5	0.57	139.1
Aug. 2010	3.27	0.005	4037.5	0.27	30.7
Sept. 2010	4.49	0.03	4900	0.19	32.4
Oct. 2010	9.19	0.024	4737.5	0.23	66.8
Nov. 2010	8.05	0.01	5792.5	0.61	128.6
Dec 2010	25.64	0.024	5142	0.59	325.6
Jan. 2011	63.93	0.021	5930	0.36	222.5
Feb. 2011	30.77	0.044	4982.5	0.39	179.5
Mar. 2011	26.32	0.017	5368	0.06	60.5
Apr. 2011	8.63	0.032	5293	0.34	59.5
May 2011	5.20	0.0178	4260	0.37	35.8
Jun. 2011	4.71	0.0336	4778	0.52	28.1
Jul. 2011	3.66	0.0124	5179	0.5	21.1
Aug. 2011	12.61	0.00286	4107	<0.25	32.3
Sept. 2011	17.57	0.0017	4528	0.49	85.7
Oct. 2011	35.89	0.0008	3438	0.56	208.3
Nov. 2011	20.60	0.003	3733	0.5	276.8
Dec. 2011	37.99	0.0126	4527	0.37	217.8
Average	**14.18**	**0.0131**	**4742**	**0.48**	**146.8**

Appendix 1: Se, Hg, B, Tl & Mn Levels in ug/L of Final Outfall in 2010-2011 at Duke Energy Facility. ***Courtesy of Duke Energy***

Month/Year	Selenium	Mercury	Boron	Thallium	Manganese
Mar. 2015	0.93	0.0016	1806.6	0.13	81.97
Apr. 2015	0.91	0.0015	1652.65	0.12	81.65
May 2015	0.86	0.0015	1698.26	0.12	58.82
Jun. 2015	0.71	<0.001	1748.25	0.17	48.91
Jul. 2015	0.72	0.0011	1837.99	0.19	27.83
Aug. 2015	0.59	<0.001	1708.30	0.16	11.74
Sept. 2015	0.58	<0.001	1714.61	0.15	14.56
Oct. 2015	0.75	<0.001	1417.90	1.09	29.86
Nov. 2015	0.72	0.0015	1676.82	0.12	38.28
Dec. 2015	0.60	0.0016	1394.31	0.13	64.55
Average	**0.74**	**0.0009**	**1665.57**	**0.24**	**45.81**

Appendix 2: Se, Hg, B, Tl & Mn Levels in ug/L of Final Outfall in 2015 at Duke Energy Facility. ***Courtesy of Duke Energy***