

## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

July 1, 2010

Illinois Environmental Protection Agency  
Attn.: Michael S. Garretson  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

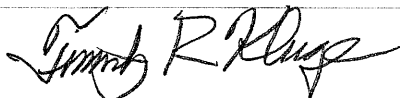
Re: NPDES Permit IL0028321  
Compliance Schedule Interim Report

Dear Mr. Garretson:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 2009-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

cc: Bob Mosher, DWPC Standards  
Rick Pinneo, DWPC Permits  
Joe Koronkowski, Champaign Region

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Sanitary District of Decatur  
Nickel and Zinc Limits  
June 2010 Interim Report**

The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires that an interim progress report be submitted to Illinois EPA by July 1, 2010. A summary of information gathered and activities since the previous report is provided below.

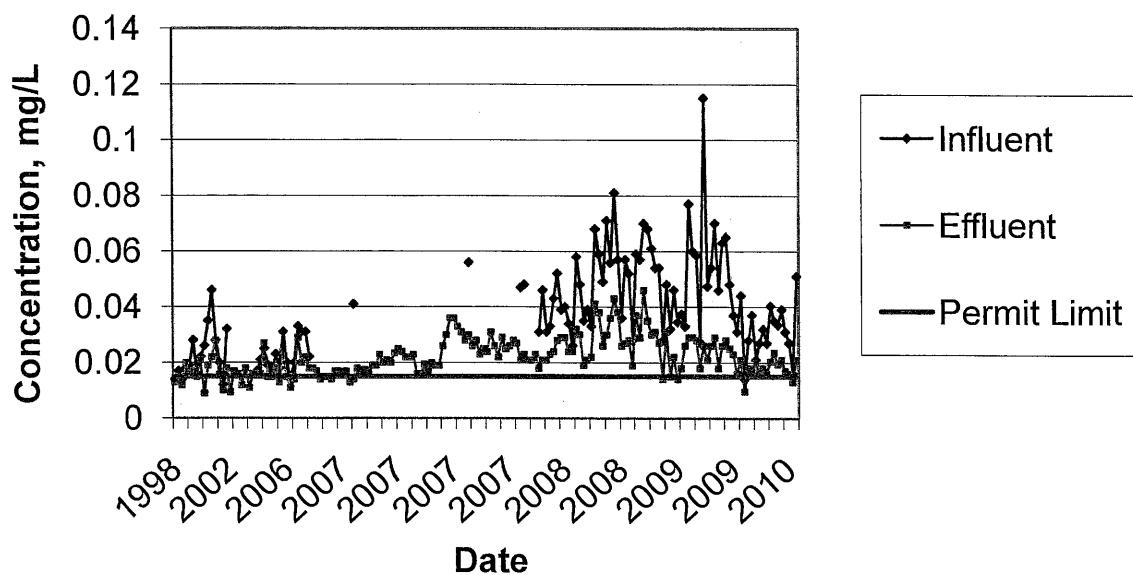
On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified to incorporate the variance.

**Plant Influent and Effluent Sampling**

Nickel and zinc have been included in quarterly plant influent and effluent sampling for many years. Ongoing influent and effluent sampling for nickel and zinc continues at a frequency of twice monthly. The District began performing metals analysis in-house in early 2009.

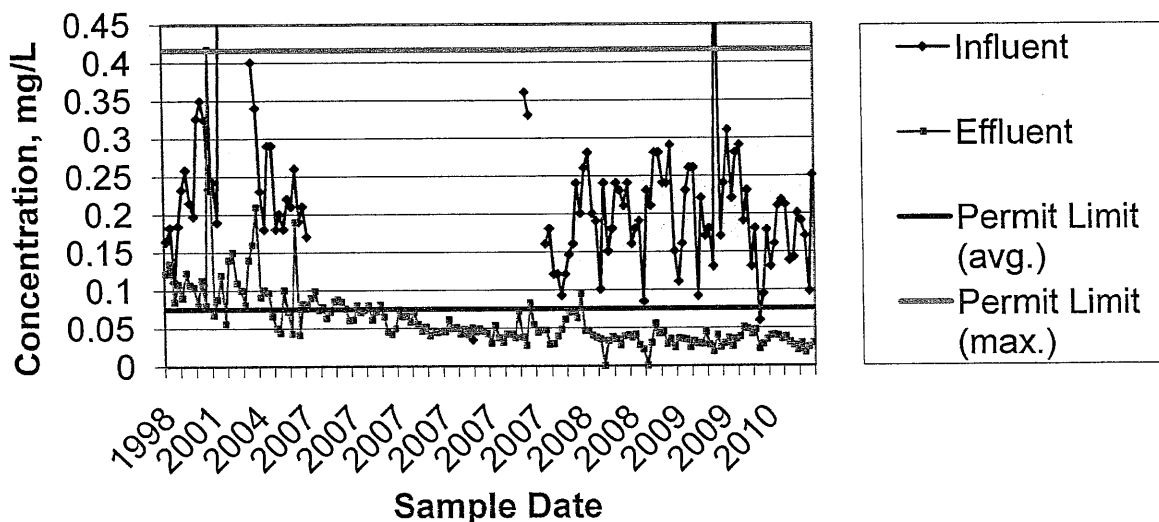
An updated summary of influent and effluent values is shown below. Review of past data shows that the plant discharge is not able to consistently meet the current nickel permit limit. Recent zinc concentrations are below the permit limit.

**Influent and Effluent Nickel**



06/30/2014 - \* \* \* R2014-024 \* \* \*

### Influent and Effluent Zinc



#### Industrial Source Sampling and Investigations

Sampling of the major industries (ADM and Tate & Lyle) for metals has been increased to twice monthly and other industries discharging metals are now sampled quarterly. Sample results obtained from the major industries within the past year are attached.

Pretreatment local limits have been calculated based on the current permit limits for nickel and zinc, and the District's Board of Trustees adopted the new limits on October 21, 2009. The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits.

Both industries formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. Investigations conducted by ADM are summarized in the District's June 15, 2009 variance petition (pages 22-31) and further in the District's September 30, 2009 response to the Agency's variance recommendation (pages 4-7). ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. The District's pretreatment permit requires semi-annual reports of ADM's investigations,

06/30/2014 - \* \* \* R2014-024 \* \* \*

and a copy of the most recent report is attached. The District and ADM have scheduled a meeting with Illinois EPA on July 8 to review these investigations in more detail.

### **Receiving Stream Sampling**

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. While the Wyckles Road sampling site is not accessible until later this summer because of bridge construction, three additional river sampling sites closer to the treatment plant outfall are being sampled. These locations are approximately 100 yards, 600 yards, and 1000 yards (Rock Springs Bicycle Trail bridge) downstream of the District's outfall. All upstream and downstream sample results during the past year have been below the Illinois water quality standard. This period has been characterized by above-normal flows in the river.

### **Water Quality Standard Investigations**

The District is continuing to investigate approaches to a water quality standard adjustment including the biotic ligand model and use of the water effect ratio. The District has contracted with HydroQual, Inc. (Dr. Robert Santore) in Syracuse, New York to conduct an evaluation of the applicability of these approaches based on available data. A preliminary summary of Dr. Santore's evaluation is attached. His evaluation indicates that a significantly higher site-specific nickel criterion could be justified based on bioavailability to aquatic organisms. This analysis is based on chemical data from the District's effluent, which contributes most or all of the Sangamon River flow during critical low flow conditions. Additional river sampling is planned during low flow conditions later this summer to verify stream concentrations.

### **Compliance Plan**

---

A proposed compliance plan and schedule is included in the Board Order granting the District's variance. The District will continue to proceed in accordance with the schedule in the Order with efforts in three areas:

1. Continuing to work with ADM to investigate nickel removal technologies, and to determine a sludge wasting plan that will minimize zinc discharges. A summary of ADM's investigations is attached. The Order lists ten technologies that are to be investigated by December 31, 2010. Also, ADM recently reported to the District that they have done some testing and found that they should be able to dry their sludge using a centrifuge followed by a belt filter press. ADM would then be able to utilize the solids in their co-generation plant or landfill the dry solids rather than wasting to the sewer.
2. Conducting additional discussions with Illinois EPA permit personnel regarding variable permit limits based on the amount of flow available in the Sangamon River. Currently, the District anticipates a proposal with three to four tiers of river flow and accompanying permit limits.

06/30/2014 - \* \* \* R2014-024 \* \* \*

3. Conducting additional discussions with Illinois EPA and U.S. EPA standards personnel regarding justification for a site-specific water quality standard for nickel, based on bioavailability. Further discussions are needed to gain initial input for possible development of a site-specific WQS proposal.

06/30/2014 - \* \* \* R2014-024 \* \* \*

**SDD Major Industrial Nickel and Zinc Results**

Date	ADM A Total Ni	ADM A Total Zn	ADM D Total Ni	ADM D Total Zn
7/6/2009	0.101	0.327	0.114	0.313
7/13/2009	0.102	0.368	0.114	0.33
8/3/2009	0.101	0.461	0.13	0.396
8/10/2009	0.106	0.454	0.132	0.433
9/1/2009	0.0971	0.496	0.127	0.415
9/8/2009	0.094	0.5	0.122	0.393
9/28/2009	0.0833	0.342	0.105	0.324
9/29/2009	0.0897	0.406	0.107	0.33
9/30/2009	0.0956	0.462	0.117	0.425
10/1/2009	0.0901	0.504	0.121	0.459
10/13/2009	0.0657	0.339	0.0981	0.237
11/9/2009	0.107	0.449	0.112	0.372
11/23/2009	0.0989	0.346	0.0719	0.203
12/1/2009	0.0899	0.291	0.079	0.213
12/7/2009	0.0899	0.358	0.0948	0.325
1/11/2010	0.0825	0.362	0.0693	0.254
2/1/2010	0.0907	0.506	0.0949	0.435
2/8/2010	0.0921	0.375	0.112	0.378
3/8/2010	0.0824	0.329	0.0897	0.203
3/15/2010	0.0621	0.522	0.11	0.303
4/5/2010	0.0649	0.441	0.107	0.309
4/12/2010	0.106	0.593	0.119	0.374
5/3/2010	0.0654	0.386	0.0958	0.258
5/10/2010	0.0551	0.333	0.0774	0.189
SDD Ordinance Limit (Avg.)	0.0365	0.45		
SDD Ordinance Limit (Max.)	0.15	1.7		

06/30/2014 - \* \* \* R2014-024 \* \* \*

Date	TLIA A Total Ni	TLIA A Total Zn	TLIA C Total Ni	TLIA C Total Zn
7/6/2009	0.0128	0.0903	0.00705	0.214
7/13/2009	0.00943	0.226	0.00593	0.0989
8/3/2009	0.0128	0.119	0.00826	0.109
8/10/2009	0.00849	0.126	0.00358	0.0833
9/1/2009	0.00717	0.0726	0.0118	0.309
9/28/2009	0.0286	0.073	0.00433	0.143
9/29/2009	0.00966	0.0763	0.0123	0.143
9/30/2009	0.0207	0.0574	0.00789	0.142
10/1/2009	0.014	0.112	0.0189	0.316
10/13/2009	0.00823	0.0915	0.00934	0.477
11/9/2009	0.0117	0.102	0.00563	0.221
12/1/2009	0.0046	0.0901	0.00233	0.0646
12/7/2009	0.00381	0.081	0.00898	0.118
1/11/2010	0.00307	0.0429	0.00598	0.453
2/1/2010	0.00392	0.112	0.00353	0.232
2/8/2010	0.00171	0.0294	0.00205	0.109
3/8/2010	0.00565	0.0752	0.00633	0.13
3/15/2010	0.00356	0.0606	0.00455	0.168
4/5/2010	0.00265	0.0354	0.00294	0.198
4/12/2010	0.0128	0.188	0.00489	0.579
5/3/2010	0.00339	0.0817	0.00479	0.234
5/10/2010	0.00429	0.107	0.00839	0.388
SDD Ordinance Limit (Avg.)	0.0365	0.45		
SDD Ordinance Limit (Max.)	0.15	1.7		

06/30/2014 - \* \* \* R2014-024 \* \* \*



COPY

June 15, 2010

Pretreatment Coordinator  
 Sanitary District of Decatur  
 501 Dipper Lane  
 Decatur, Illinois 62522

RECEIVED

JUN 18 2010

SANITARY DISTRICT  
 OF DECATUR

Re: Interim Nickel and Zinc Report

Dear Sir,

Per Special Condition E.8. of Industrial Discharge Permit #200, we are submitting this summary of our research efforts to reduce nickel and zinc in our effluent. To date we have investigated the following:

1) Status of Anaerobic TSS Carry-over

- Anaerobic TSS carry-over and microbiologist findings  
 Effect of changes recommended by consultant.

2) Ongoing Nickel Reduction Work w/ outside companies

- Bench work at the start-up company's site w/ treated clay is on-going. Latest results erratic.
- Inorganic substrate with attached ligand/skeleton using nanotechnology. Latest results promising.  
 Work is on-going at start-up company's site. A 2nd Decatur visit is planned.
- Very small, water dispersable nano particles; nano-IX.  
 Testing at start-up company's site is on-going. Very little promise, so far.
- Liquid chemistry said to be 'green'. Apparently a 2 step process that can utilize a DAF unit.  
 2nd lengthy study completed. Process does not look as promising as originally hoped.
- Current ADM-contracted water treatment company has their Research team involved.  
 Nothing of interest at this point.
- Two more water treatment companies have received samples and performed tests.  
 Metal precipitant is currently under initial testing at ADM.

3) RO Pilot Work

- Long-expected proposal from GE Betz for 100gpm UF & RO test skid did not pan out.  
 Looking elsewhere



06/30/2014 - \* \* \* R2014-024 \* \* \*



4) Internal ADM Lab Work

- Performed tests based on a patent for inorganic substrate used to concentrate trace materials in pollutant testing. Not promising.
  
- Dry product, metal precipitant. Did not function well.
  
- Series of tests were performed using a combination of flocculants, polymers and coagulants. About 0.065ppm was the lowest soluble Ni attained.
  
- Diatomaceous earth-based, specially treated material can meet the Ni limit w/ Low Salt dilution. Not affordable w/o regeneration, which has not been done before. Will try their liquid version.
  
- A Dow adsorbent (de-colorizing resin) will meet the Ni limit with Low Salt dilution. Isotherm data has been collected & Dow performed vessel size & cycle time calculations. Problematic regeneration. Very expensive resin. Nickel waste requires RO treatment. We're waiting on Dow's final cost calculations to see if a column pilot study is warranted.
  
- Metal precipitant blend utilizing some DTC will meet the Ni limit w/ Low Salt dilution. Minimum dose studies have been performed. Another attempt being made to tie up residual DTC. Expect results in <2 weeks.

As you are aware, we are pursuing many options and will keep you apprised of our progress, and which technologies show the most promise. Feel free to contact me if you have any questions regarding this summary.

Respectfully submitted,

A handwritten signature in black ink that reads "Mark Carroll". The signature is written in a cursive, flowing style.

Mark Carroll  
Environmental Compliance Manager  
ADM Decatur Corn Processing Plant

# Estimate of BLM Adjustment to Ni Criterion for Decatur Sanitation District

Robert Santore  
HydroQual, Inc



March 30, 2010

Preliminary results, Please do not cite or distribute

1

## Outline

- Estimated downstream water quality
- Predicted toxicity to *Daphnia magna*
  - Example use as a WER test organism
- Predicted estimate of WQC

March 30, 2010

Preliminary results, Please do not cite or distribute

2

06/30/2014 - \* \* \* R2014-024 \* \* \*

## Supplied info

Plant Final Effluent									
Sampling Date	Sodium	Potassium	Calcium	Magnesium	pH	Alkalinity	Sulfate	Chloride	Carbonaceous BOD <sub>5</sub>
	Total (mg/L)	Total (mg/L)	Total (mg/L)	Total (mg/L)					
11/13/2008	520	130	54	64	7.82	359		631	< 2.0
11/18/2008					7.63	357	521		< 2.0
11/20/2008					7.86	332		635	2.4
11/25/2008					7.68	315	333		2.0
11/26/2008					7.81	337		712	
11/27/2008									2.0
12/2/2008					7.76	422	283		< 2.0
12/4/2008	500		53	59	7.73	396		651	2.5
12/9/2008					7.58	357	366		2.6
12/11/2008					7.55	344		524	< 2.0
12/16/2008					7.60	379	315		< 2.0
12/18/2008			58	59	7.80	376		660	< 2.0

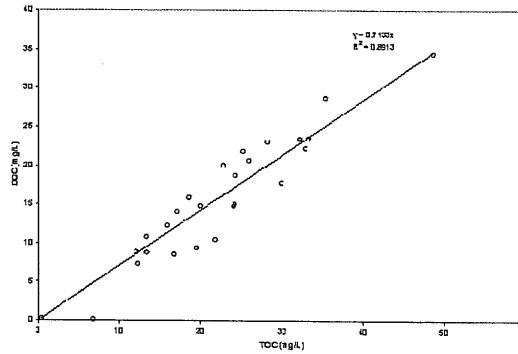
Hardness 390

March 30, 2010

Preliminary results, Please do not cite or distribute

3

## Estimation of DOC



NYSDEC CARP project  
[www.dec.state.ny.us/website/dow/bwam/CARP](http://www.dec.state.ny.us/website/dow/bwam/CARP).

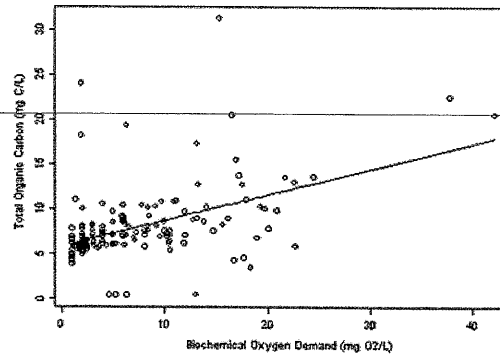
March 30, 2010

Preliminary results, Please do not cite or distribute

4

## Estimation of TOC

TOCavg ~ BODavg (All Samples)



Monitoring data from all major POTWs reporting TOC and 5-day BOD in the United States were downloaded from the PCS web site, [www.epa.gov/enviro/html/pcs/adhoc.html](http://www.epa.gov/enviro/html/pcs/adhoc.html).

March 30, 2010

Preliminary results, Please do not cite or distribute

5

## Method 1 – Calculate WER

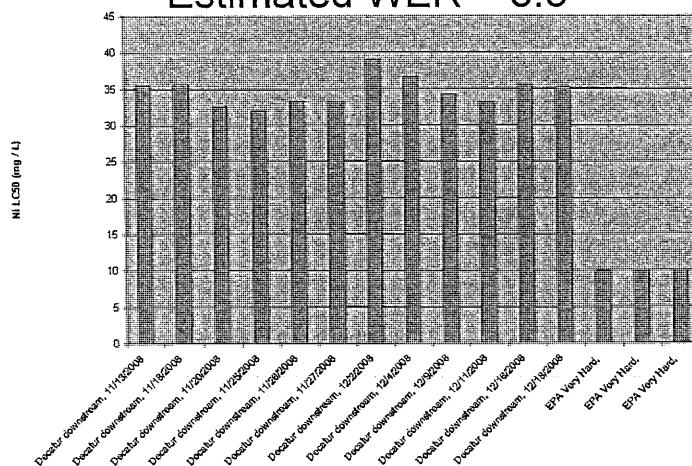
- Use the BLM to estimate Ni toxicity to a sensitive aquatic organism suitable for use in a WER study
- Site water will be characterized by the provided chemistry, along with estimated DOC from BOD
- Reference water will be standard EPA recipe
- $WER = (\text{Site Water LC50}) / (\text{Reference LC50})$

March 30, 2010

Preliminary results, Please do not cite or distribute

6

## BLM Estimated Ni toxicity to *D magna* Estimated WER = 3.5



7

## Estimated WER

- The acute standard in IL  
CMC =  $e(0.8460[\ln(\text{hardness})] + 0.5173)$ 
  - At a hardness of 390, CMC = 261  $\mu\text{g/L}$
  - Adjusted by WER, SSCMC = 913  $\mu\text{g/L}$
- The chronic (geomean) standard in IL  
FCV =  $e(0.8460[\ln(\text{hardness})] - 1.865)$ 
  - At a hardness of 390, FCV = 14  $\mu\text{g/L}$
  - Adjusted by WER, SSFCV = 84  $\mu\text{g/L}$

March 30, 2010

Preliminary results, Please do not cite or distribute

8

## Method 2 – Use the BLM to estimate SSWQC

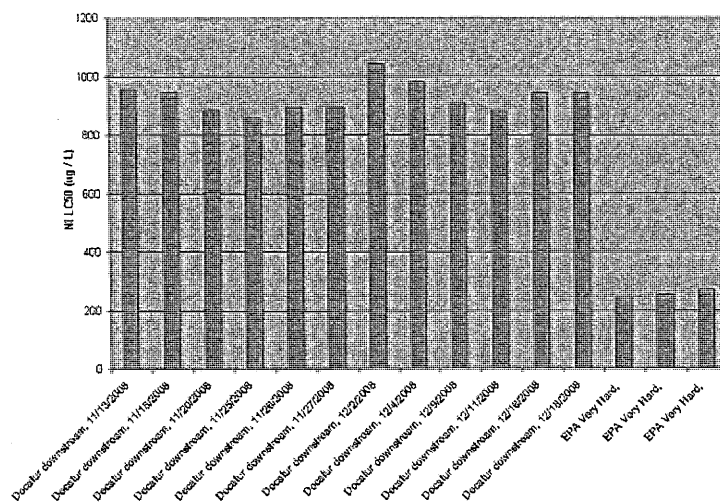
- The BLM was adjusted to match the CMC at a hardness of 50 in a typical test water (e.g., standard EPA recipe)
- Application of the BLM to waters with higher hardness and DOC can then estimate a site-specific WQC

March 30, 2010

Preliminary results, Please do not cite or distribute

9

## BLM Estimated Ni CMC



10

## Summary and Conclusions

- Downstream water quality was estimated from effluent characteristics (personal communication from T. Kluge, the downstream water is effluent dominated and frequently there is no other flow upstream of discharge)
- The Ni BLM was used to estimate downstream Ni criteria in two ways, using both a WER approach, and using a direct estimate of the CMC
- Both approaches yielded similar results, suggesting that a site-specific criterion for Ni will be considerably higher than the default value used for the state

March 30, 2010

Preliminary results, Please do not cite or distribute

11



06/30/2014 10:29:33 AM

## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

December 29, 2010

Illinois Environmental Protection Agency  
Attn.: Michael S. Garretson  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

Re: NPDES Permit IL0028321  
IPCB Order PCB 09-125  
Interim Report

Dear Mr. Garretson:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 09-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Sanitary District of Decatur  
Nickel and Zinc Limits  
December 2010 Interim Report**

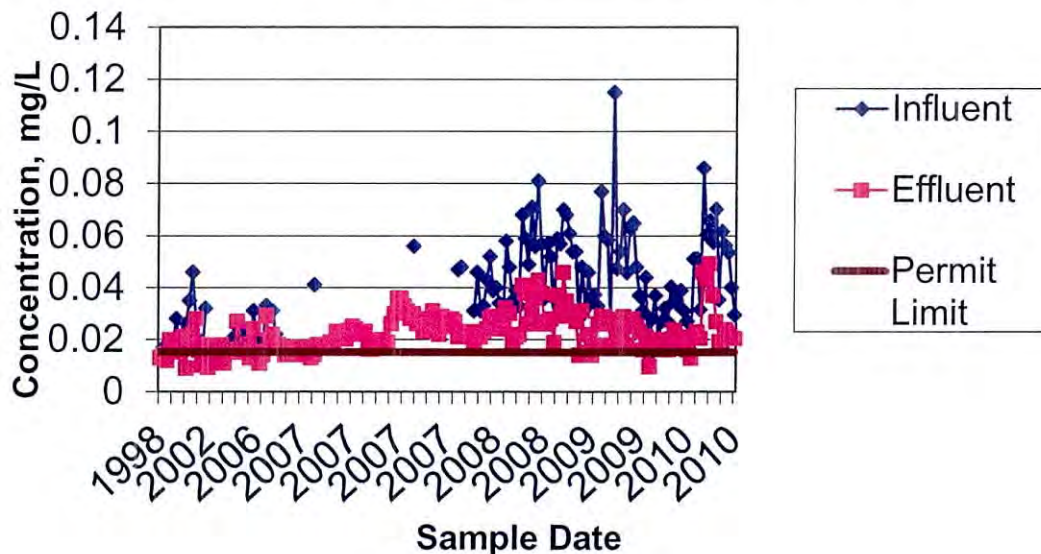
The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires that an interim progress report be submitted to Illinois EPA by January 1, 2011.

On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified to incorporate the variance. The Board Order also requires that an interim progress report be submitted by January 1, 2011 and lists a number of other activities and investigations that are to be completed. This report is submitted to meet both the permit and variance requirements.

**Plant Influent and Effluent Sampling**

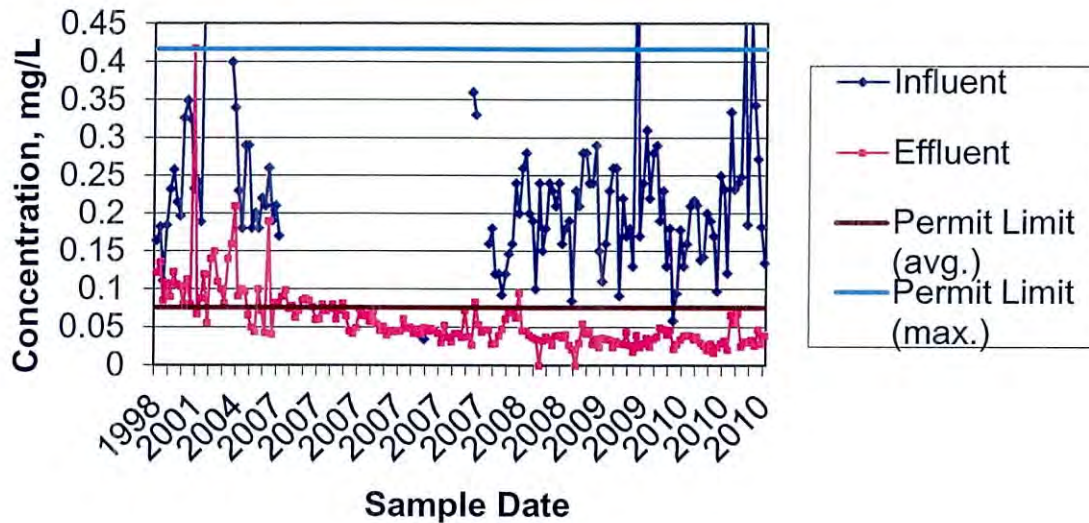
Ongoing influent and effluent sampling for nickel and zinc continues at a frequency of twice monthly. An updated summary of influent and effluent values is shown below. Past data shows that the plant effluent is not able to consistently meet the current nickel permit limit. Zinc concentrations remain below the permit limit.

**Influent and Effluent Nickel**



06/30/2014 - \* \* \* R2014-024 \* \* \*

## Influent and Effluent Zinc



### Receiving Stream Sampling

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. One upstream and four downstream sampling sites are being monitored. All upstream and downstream zinc results during the past year have been below the Illinois water quality standard. Downstream nickel concentrations during the relatively dry fall weather in 2010 reflected effluent concentrations with minimal upstream dilution available. A summary of 2010 river monitoring data is attached.

### Pretreatment Ordinance Limits

The District's pretreatment ordinance was amended in October 2009 as noted in previous reports.

### Stream Flow-Based Compliance Options

The District continues investigation of flow-based permit limits, to take advantage of upstream flow for mixing when it is available. This concept could potentially allow a savings in treatment facility operating costs when the upstream flow is sufficient to meet water quality standards after mixing with treatment plant effluent. A USGS flow gaging station is located about two miles upstream of the District's discharge point, and provides near- real time flow information. We are currently developing a proposal that would establish three to four tiers of limits based on ranges of upstream flow, providing an administratively straightforward way to define and evaluate permit compliance. Informal discussions with Illinois EPA personnel have indicated that the concept of flow-based

06/30/2014 - \* \* \* R2014-024 \* \* \*

limits could be considered. We expect to have a proposal for presentation to Illinois EPA early in 2011, to be followed at a later time with a permit modification request.

### **Water Quality Standard Investigations**

The District is continuing to investigate approaches to a water quality standard adjustment including the biotic ligand model (BLM) and use of the water effect ratio. Additional river sampling was conducted during low flow conditions later this summer to verify stream concentrations. On December 9, discussions were initiated with U.S. EPA and Illinois EPA on the reaction to a bioavailability approach. Personnel from U.S. EPA indicated that they would like to review published information on the nickel BLM and a follow-up call is anticipated in early January 2011. The District anticipates preparation of a petition for a site-specific nickel standard to occur in the first half of 2011.

The District has also been notified by Illinois EPA of a possible revision of the zinc water quality standard, based on an error discovered in the derivation of the current standard. We are currently evaluating the impact of this possible change on the District's zinc pretreatment ordinance limit.

### **Industrial Source Sampling and Investigations**

Sampling of the major industries (ADM and Tate & Lyle) for metals continues at a frequency of twice monthly and other industries discharging metals are sampled quarterly. Sample results obtained from the major industries within the past year are attached.

The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits. Final local limits will be effective upon expiration of the District's variance.

Both major industries formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. The District's pretreatment permit requires semi-annual reports of ADM's investigations, and a copy of the most recent report is attached. The report includes status updates on the specific treatment technologies required to be investigated. District staff met with ADM on December 22, 2010 to review the information in the report.

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Additional Pretreatment Limit Investigations**

Pretreatment ordinance limits adopted in 2009 were adopted as total (rather than soluble) limits based on review of soluble/insoluble data. Refinement of pretreatment limits is an ongoing process and will depend on final permit limits as well as treatment technologies that might be employed by industrial users. The required determination of soluble/insoluble vs. total limits will be updated as part of the final compliance plan submitted to the Agency.

**Compliance Plan**

In summary, the District's proposed compliance plan includes ongoing work as required by the Board Order granting the District's variance. The District will continue to proceed in accordance with the schedule in the Order with efforts in three areas:

1. Continuing to work with ADM to investigate nickel removal technologies, and to determine a sludge wasting plan that will minimize zinc discharges. The Order lists ten technologies that are to be investigated by December 31, 2010, and the summary documents work on all ten as required.
2. Conducting additional discussions with Illinois EPA permit personnel regarding variable permit limits based on the amount of flow available in the Sangamon River. As noted above, Illinois EPA has been receptive to this concept. Additional evaluations are underway to possibly extend the concept to other parameters. The District plans to submit a comprehensive proposal to Illinois EPA during the first half of 2011.
3. Conducting additional discussions with Illinois EPA and U.S. EPA standards personnel regarding justification for a site-specific water quality standard for nickel, based on bioavailability. As noted above, development of a petition for the Pollution Control Board is planned in the first half of 2011.

06/30/2014 - \*\*\* R2014-024 \*\*\*

## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

June 29, 2011

Illinois Environmental Protection Agency  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

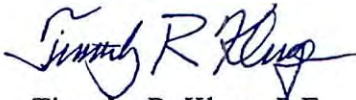
Re: NPDES Permit IL0028321  
IPCB Order PCB 09-125  
Interim Report

Dear Sir or Madam:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 09-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

cc: Rick Pinneo, IEPA (via email)  
Bob Mosher, IEPA (via email)

06/30/2014 - \* \* \* R2014-024 \* \* \*

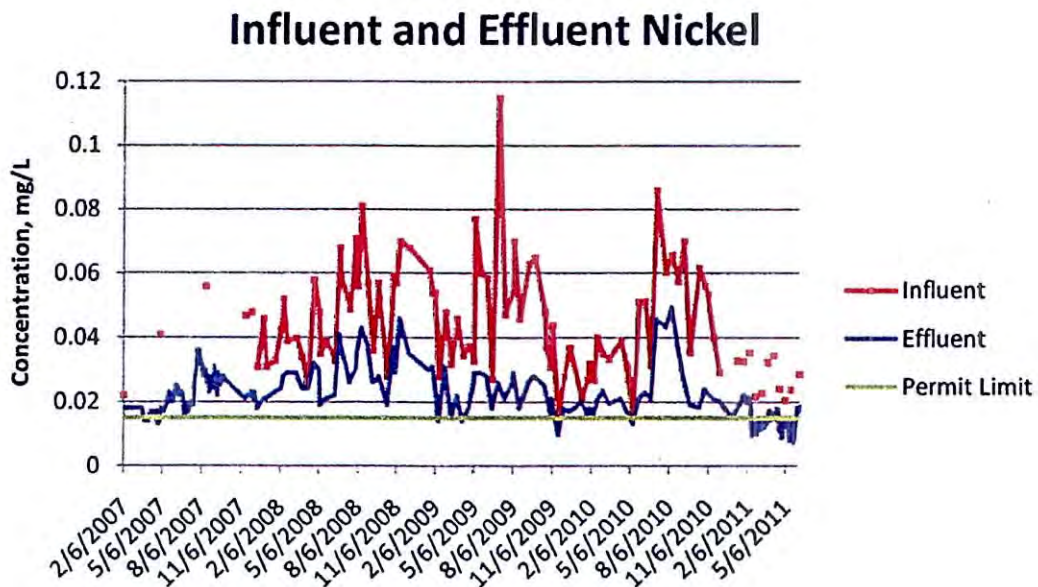
**Sanitary District of Decatur  
Nickel and Zinc Limits  
June 2011 Interim Report**

The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires that an interim progress report be submitted to Illinois EPA by July 1, 2011.

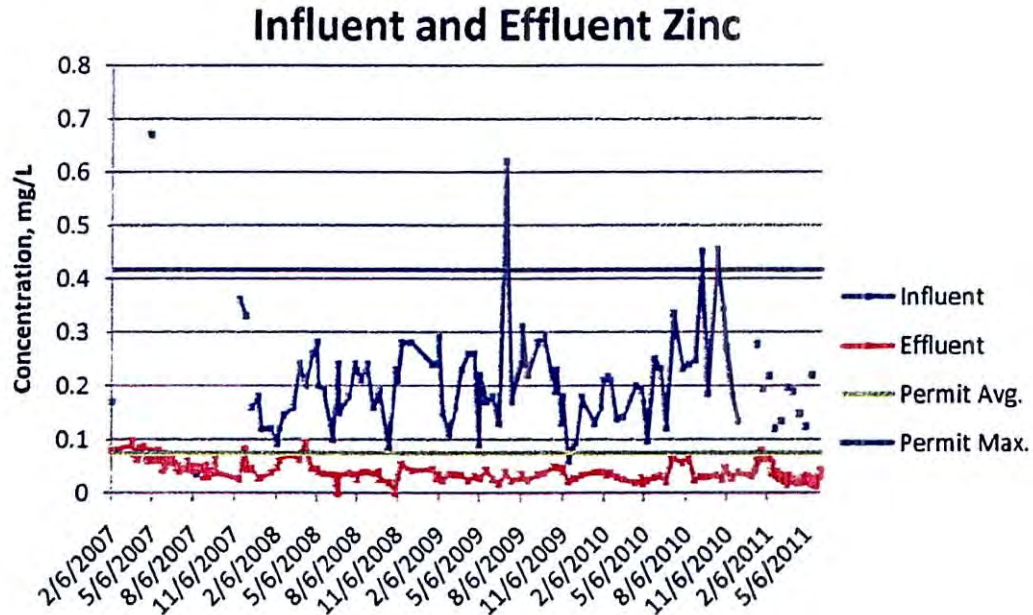
On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified to incorporate the variance although Illinois EPA issued a Public Notice and draft modified permit on May 26, 2011. The Board Order also requires that an interim progress report be submitted by July 1, 2011 and lists a number of other activities and investigations that are to be completed. This report is submitted to meet both the permit and variance requirements.

**Plant Influent and Effluent Sampling**

Ongoing influent and effluent sampling for nickel and zinc continues at a frequency of twice monthly. An updated summary of influent and effluent values is shown below. Past data shows that the plant effluent is not able to consistently meet the current nickel permit limit. Influent and effluent nickel concentrations in the first half of 2011 have been lower than in previous years, due to reduced loadings from ADM. According to ADM personnel, variations in product mix or in year-to-year differences in grain may be a factor in the reduction. Zinc concentrations remain below the permit limit.



06/30/2014 - \* \* \* R2014-024 \* \* \*



#### Receiving Stream Sampling

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. One upstream and four downstream sampling sites are being monitored. A summary of 2010-2011 river monitoring data is attached. All upstream and downstream zinc results during 2011 have been below the Illinois water quality standard.

#### Pretreatment Ordinance Limits

The District's pretreatment ordinance was amended in October 2009 as noted in previous reports.

#### Stream Flow-Based Compliance Options

The District continues investigation of flow-based permit limits, to take advantage of upstream flow for mixing when it is available. This concept could potentially allow a savings in treatment facility operating costs when the upstream flow is sufficient to meet water quality standards after mixing with treatment plant effluent. A USGS flow gauging station is located about two miles upstream of the District's discharge point, and provides near- real time flow information. We are continuing to develop a proposal that would establish limits based on upstream flow, with a goal of providing an administratively straightforward way to define and evaluate permit compliance. Informal discussions with Illinois EPA personnel have indicated that the concept of flow-based limits could be



06/30/2014 - \* \* \* R2014-024 \* \* \*

considered. We expect to have a proposal for presentation to Illinois EPA in the second half of 2011, for consideration during renewal of our NPDES permit in 2012.

### **Water Quality Standard Investigations**

The District is continuing to investigate approaches to a water quality standard adjustment including prediction of a water effect ratio using the biotic ligand model (BLM). On December 9, 2010 discussions were initiated with U.S. EPA and Illinois EPA on the reaction to a bioavailability approach. Personnel from U.S. EPA indicated that they would like to review published information on the nickel BLM and also requested information on how variability in discharge parameters would affect the predicted toxicity. Variability information was compiled and reviewed prior to discussion in a follow-up call on June 6. The District anticipates a petition for a site-specific nickel standard will be filed with the Pollution Control Board in the second half of 2011.

We are also following the Pollution Control Board rulemaking currently underway to correct an error found in the existing zinc water quality standard.

### **Industrial Source Sampling and Investigations**

Sampling of the major industries (ADM and Tate & Lyle) for metals continues at a frequency of twice monthly and other industries discharging metals are sampled quarterly. Sample results obtained from the major industries within the past year are attached.

The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits. Final local limits will be effective upon expiration of the District's variance.

Both major industries formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. District staff met with ADM personnel several times during the first half of 2011, most recently on May 31. The District's pretreatment permit requires semi-annual reports of ADM's investigations, and a report will be provided to Illinois EPA during our meeting scheduled for July 7. Work during the past six months has included pilot testing for several nickel removal technologies, toxicity testing to determine

06/30/2014 - \* \* \* R2014-024 \* \* \*

potential impacts of the District's nitrification process, and ongoing research into alternative technologies.

### **Additional Pretreatment Limit Investigations**

Pretreatment ordinance limits adopted in 2009 were adopted as total (rather than soluble) limits based on review of soluble/insoluble data. Refinement of pretreatment limits is an ongoing process and will depend on final permit limits as well as treatment technologies that might be employed by industrial users. The required determination of soluble/insoluble vs. total limits will be updated as part of the final compliance plan submitted to the Agency.

### **Chronic Toxicity Testing**

Chronic whole effluent toxicity testing was performed on the District's discharge in July, September, and December 2007. The test results were forwarded to Illinois EPA and reviewed in 2008. A number of inconsistencies were found in the test results and in the interpretation of the results by the laboratory. Because of the inconsistencies and to obtain current data, a new round of chronic toxicity testing will be performed in the second half of 2011.

### **Compliance Plan**

In summary, the District's proposed compliance plan includes ongoing work as required by the Board Order granting the District's variance. The District will continue to proceed in accordance with the schedule in the Order with efforts in three areas:

1. Continuing to work with ADM to investigate nickel removal technologies, and to determine a sludge wasting plan that will minimize zinc discharges. The Order lists ten technologies that were to be investigated by December 31, 2010, the the investigations were done as required. Additional investigations continue and a summary will be provided to Illinois EPA.
2. Conducting additional discussions with Illinois EPA permit personnel regarding variable permit limits based on the amount of flow available in the Sangamon River. As noted above, Illinois EPA has been receptive to this concept. The District plans to submit a comprehensive proposal to Illinois EPA during the second half of 2011.
3. Conducting additional discussions with Illinois EPA and U.S. EPA standards personnel regarding justification for a site-specific water quality standard for nickel, based on bioavailability. As noted above, development of a petition for the Pollution Control Board is planned in the first half of 2011.

06/30/2014 - \* \* \* R2014-024 \* \* \*

SDD Major Industrial Nickel and Zinc Results				
	ADM Point A	ADM Point A	ADM Point D	ADM Point D
Sample	Nickel, Tot	Zinc, Tot	Nickel, Tot	Zinc, Tot
Date	mg/L	mg/L	mg/L	mg/L
6/1/2010	0.0813	0.488	0.12	0.441
6/14/2010	0.0826	0.453	0.104	0.345
7/8/2010	0.148	0.54	0.283	1.07
7/12/2010	0.144	0.528	0.193	0.514
8/2/2010	0.125	0.457	0.172	0.446
8/9/2010	0.126	0.44	0.184	0.474
9/1/2010	0.0766	0.465	0.122	0.469
9/20/2010	0.0744	0.442	0.121	0.649
10/4/2010	0.0781	0.461	0.0938	0.369
10/14/2010	0.162	1.18	0.179	1.18
11/8/2010	0.0524	0.24	0.0646	0.208
11/23/2010	0.13	0.665	0.122	0.413
12/6/2010	0.0715	0.53	0.131	0.581
12/13/2010	0.0649	0.498	0.0774	0.219
1/5/2011	0.0629	0.53	0.0669	0.204
1/10/2011	0.0577	0.495	0.0666	0.188
2/7/2011	0.0836	0.756	0.0892	0.329
2/14/2011	0.0589	0.472	0.0598	0.18
3/7/2011	0.0773	0.447	0.0627	0.128
3/14/2011	0.086	0.51	0.1	0.449
4/4/2011	0.07	0.428	0.0841	0.387
4/20/2011	0.0687	0.33	0.0861	0.347
5/2/2011	0.0712	0.304	0.0809	0.302
5/9/2011	0.06	0.301	0.0712	0.3
SDD Ordinance Limit (Avg.)	0.0365	0.45		
SDD Ordinance Limit (Max.)	0.15	1.7		

Sanitary District of Decatur  
Nickel and Zinc River Data 2010-2011

06/30/2014 - \* \* \* R2014-024 \* \* \*

Sample Date	Plant Final Effluent Nickel mg/L	River Up-stream Nickel mg/L	River 100 yds Down-stream Nickel mg/L	River 600 yds Down-stream Nickel mg/L	Steven's Creek Nickel mg/L	River Rock Springs Bridge Nickel mg/L	River Wyckle's Road Nickel mg/L	River Lincoln H'stead Nickel mg/L	Plant Final Effluent Zinc mg/L	River Up-stream Zinc mg/L	River 100 yds Down-stream Zinc mg/L	River 600 yds Down-stream Zinc mg/L	Steven's Creek Zinc mg/L	River Rock Springs Bridge Zinc mg/L	River Wyckle's Road Zinc mg/L	River Lincoln H'stead Nickel mg/L	Plant Final Effluent Flow mgd	River Up-stream Flow ft <sup>3</sup> /sec
1/14/10	0.0202	<0.00131	0.00374	0.00407	<0.00131	0.00331		0.00318	0.0393	<0.00660	0.0102	0.0108	<0.00660	0.00839		0.0112	30.29	208
1/28/10	0.0160	0.00205	0.00253	0.00240	<0.00131	0.00209		0.00237	0.0399	0.0129	0.0130	0.0121	0.00773	0.0135		0.0138	42.87	3470
2/11/10	0.0204	<0.00131	0.00462	0.00357	<0.00131	0.00277		0.00253	0.0344	<0.00660	0.0119	0.00980	0.00789	0.0108		0.00710	31.39	517
2/18/10	0.0304	<0.00131	0.00527	0.00468	<0.00131	0.00398		0.00351	0.0377	0.00696	0.0103	0.0103	0.00790	0.00777		0.00819	33.12	436
3/4/10	0.0235	<0.00131	0.00376	0.00332	<0.00131	0.00242		0.00240	0.0304	0.00667	0.00918	0.00851	<0.00660	0.00746		0.00895	37.82	755
3/18/10	0.0194	0.00133	0.00232	0.00199	<0.00131	0.00165		0.00200	0.0260	0.00781	0.00966	0.00953	0.00739	0.00801		0.0107	39.45	2160
4/15/10	0.0208	<0.00131	0.00290	0.00279	<0.00131	0.00237		0.00281	0.0204	<0.00660	0.00758	0.00867	<0.00660	<0.00660		0.00761	35.89	482
4/29/10	0.0173	<0.00131	0.00186	0.00201	<0.00131	0.00175		0.00222	0.0290	0.00776	0.00676	0.00833	0.0136	<0.00660		0.00902	31.86	728
5/13/10	0.0127	0.00137	0.00195	0.00244	0.00176	0.00174		0.00229	0.0244	0.00762	0.00767	0.00791	0.0121	0.00821		0.0112	38.27	1440
5/27/10	0.0211	<0.00131	0.00388	0.00284	0.00158	0.00226		0.00259	0.0293	0.00765	0.00875	0.00763	0.00872	0.00697		0.00982	37.01	948
6/10/10	0.0229	0.00205	0.00298	0.00241	0.00325	0.00217		0.00291	0.0328	0.0108	0.0106	0.00988	0.0183	0.0105		0.0145	38.57	1820
6/24/10	0.0205	0.00262	0.00620	0.00386	0.00332	0.00311		0.00345	0.0212	0.0144	0.0137	0.0125	0.0174	0.0142		0.0148	72.13	6120
7/8/10	0.0458	<0.00131	0.00637	0.00713	<0.00131	0.00540		0.00571	0.0662	<0.00660	0.0148	0.0175	<0.00660	0.0155		0.0121	34.86	348
7/29/10	0.0433	0.00190	0.00744	0.00600	0.00151	0.00580		0.00600	0.0564	0.00909	0.0132	0.0122	<0.00660	0.0123		0.0248	38.86	285
8/12/10	0.0493	0.00157	0.0367	0.0353	<0.00131	0.0327		0.0338	0.0681	0.0130	0.0578	0.0529	<0.00660	0.0480		0.0601	31.89	24
8/26/10	0.0370	0.0025	0.0319	0.0320	0.00177	0.0294		0.0211	0.0253	0.0130	0.0255	0.0246	<0.00660	0.0221		0.0121	30.59	4.7
9/9/10	0.0269	<0.00131	0.0203	0.0197	0.00135	0.0166		0.0119	0.0314	<0.00660	0.0219	0.0209	0.0113	0.0257		0.0218	32.10	11
9/23/10	0.0192	0.00186	0.0136	0.0132	0.00188	0.00915		0.0108	0.0309	0.0119	0.0590	0.0249	0.0105	0.0188		0.0162	34.19	2.0
10/14/10	0.0182	0.00251	0.0176	0.0182	0.00143	0.0149	0.0152		0.0335	0.00827	0.0335	0.0317	0.00893	0.0259	0.0303		25.66	1.9
10/28/10	0.0238	0.00135	0.0209	0.0212	<0.00131	0.0158	0.0157		0.0261	<0.00660	0.0316	0.0232	<0.00660	0.0179	0.0190		28.28	1.9
11/04/10	0.0227	0.00146	0.0222	0.0223	<0.00131	0.0193	0.0193		0.0474	<0.00660	0.0440	0.0421	<0.00660	0.0367	0.0354		31.01	2.7
11/18/10	0.0207	0.00131	0.0191	0.0189	<0.00131	0.0164	0.0170		0.0287	<0.00660	0.0271	0.0274	<0.00660	0.0245	0.0238		29.94	4.5
12/02/10	0.0203	0.00180	0.00269	0.00217	<0.00131	0.00217	0.00186		0.0396	<0.00660	0.00702	0.00745	<0.00660	0.00779	<0.00660		33.60	1480
12/16/10	0.0199	<0.00131	0.00311	0.00210	<0.00131	0.0017	0.00156		0.0356	<0.00660	0.00672	0.00859	<0.00660	<0.00660	<0.00660		28.51	694
01/13/11	0.0181	<0.00131	0.00519	0.00495	<0.00131	0.00426	0.00504		0.0503	<0.00660	0.0157	0.0152	<0.00660	0.0133	0.0149		29.48	121
01/27/11	0.0218	<0.00131	0.0144	0.0138	<0.00131	0.0113	0.0102		0.0773	<0.00660	0.0504	0.0481	<0.00660	0.0394	0.0350		30.71	3.9
02/10/11	0.0214	<0.00131	0.0141	0.0128	<0.00131	0.0112	0.00971		0.0701	<0.00660	0.0460	0.0413	0.00761	0.0364	0.0313		27.94	5.4
02/24/11	0.0132	0.00160	0.00242	0.00252	0.00150	0.00214	0.00205		0.0406	0.00841	0.0106	0.0108	0.0138	0.0114	0.00992		44.38	1970
3/10/11	0.0123	0.00169	0.00194	0.00198	0.00153	0.00184	0.00208		0.0321	0.00972	0.00978	0.00992	0.0103	0.00974	0.0100		47.51	2900
3/24/11	0.0132	<0.00131	0.00133	0.00133	<0.00131	<0.00131	<0.00131		0.0161	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660		33.28	667
4/7/11	0.0163	<0.00131	0.00343	0.00252	<0.00131	0.00241	0.00237		0.0246	<0.00660	0.00884	0.00689	<0.00660	0.00732	0.00691		30.62	326
4/21/11	0.0118	<0.00131	0.00236	0.00195	0.00254	0.00157	0.00188		0.0215	0.00729	0.00878	0.00822	0.0170	0.00939	0.00934		52.22	2540
5/5/11	0.0147	0.00177	0.00279	0.00238	0.00137	0.00218	0.00223		0.0295	<0.00660	0.00932	0.00862	<0.00660	0.00760	0.00898		41.88	1670
5/19/11	0.0125	<0.00131	0.00211	0.00186	<0.00131	0.00153	0.00150		0.0213	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	0.00777		32.29	1290
6/9/11	0.0187	<0.00131	0.00143	0.00194	0.00183	0.00162	0.00177		0.0434	<0.00660	<0.00660	0.00672	<0.00660	<0.00660	0.0124			1540

Bridge at Wyckle's Road closed for repair August 2009.

Indicates that effluent or river/creek sample concentration exceeds chronic water quality value

000137

Exhibit 13

# Estimate of BLM Adjustment to Ni Criterion for Decatur Sanitation District

Robert Santore  
HydroQual, Inc



# Outline

- *Background on Ni BLM development*
- BLM results with measured water quality
- Predicted toxicity to *Daphnia magna*
  - Example use as a WER test organism
- *Sensitivity to variation in water chemistry*
- Predicted estimate of WQC
- *Conclusions*

# Water Environment Research Federation (WERF) report 01-ECO-10T



The image shows the cover of a report from the Water Environment Research Foundation (WERF). The top section features the WERF logo in a stylized, blocky font, with the words 'WATER ENVIRONMENT' on the first line and 'RESEARCH FOUNDATION' on the second line. Below the logo, the word 'Ecosystems' is written in a smaller font within a white rectangular box. The middle section of the cover is a collage of three black and white photographs: a large pipe with a valve, a worker in a hard hat operating machinery, and a close-up of a pipette tip over a petri dish. The bottom section of the cover contains the title 'Development of a Biotic Ligand Model For Nickel: Phase I' in a serif font.

WATER ENVIRONMENT  
RESEARCH FOUNDATION

Ecosystems

Development of a Biotic Ligand  
Model For Nickel: Phase I

# Collaborative laboratory study for validation of Ni BLM



Environmental Toxicology and Chemistry, Vol. 23, No. 3, pp. 691–696, 2004  
© 2004 SETAC  
Printed in the USA  
0730-7268/04 \$12.00 + .00

## ACUTE AND CHRONIC TOXICITY OF NICKEL TO A CLADOCERAN (*CERIODAPHNIA DUBIA*) AND AN AMPHIPOD (*HYALELLA AZTECA*)

JAMES KEITHLY,\*† JOHN A. BROOKER,† DAVID K. DEFOREST,† BENJAMIN K. WU,‡ and KEVIN V. BRIX§

†Parametrix, 5808 Lake Washington Boulevard Northeast, Suite 200, Kirkland, Washington 98033, USA

‡HydroQual, 1200 MacArthur Boulevard, First Floor, Mawah, New Jersey 07430, USA

§EcoTox, 721 Navarre Avenue, Coral Gables, Florida 33134, USA

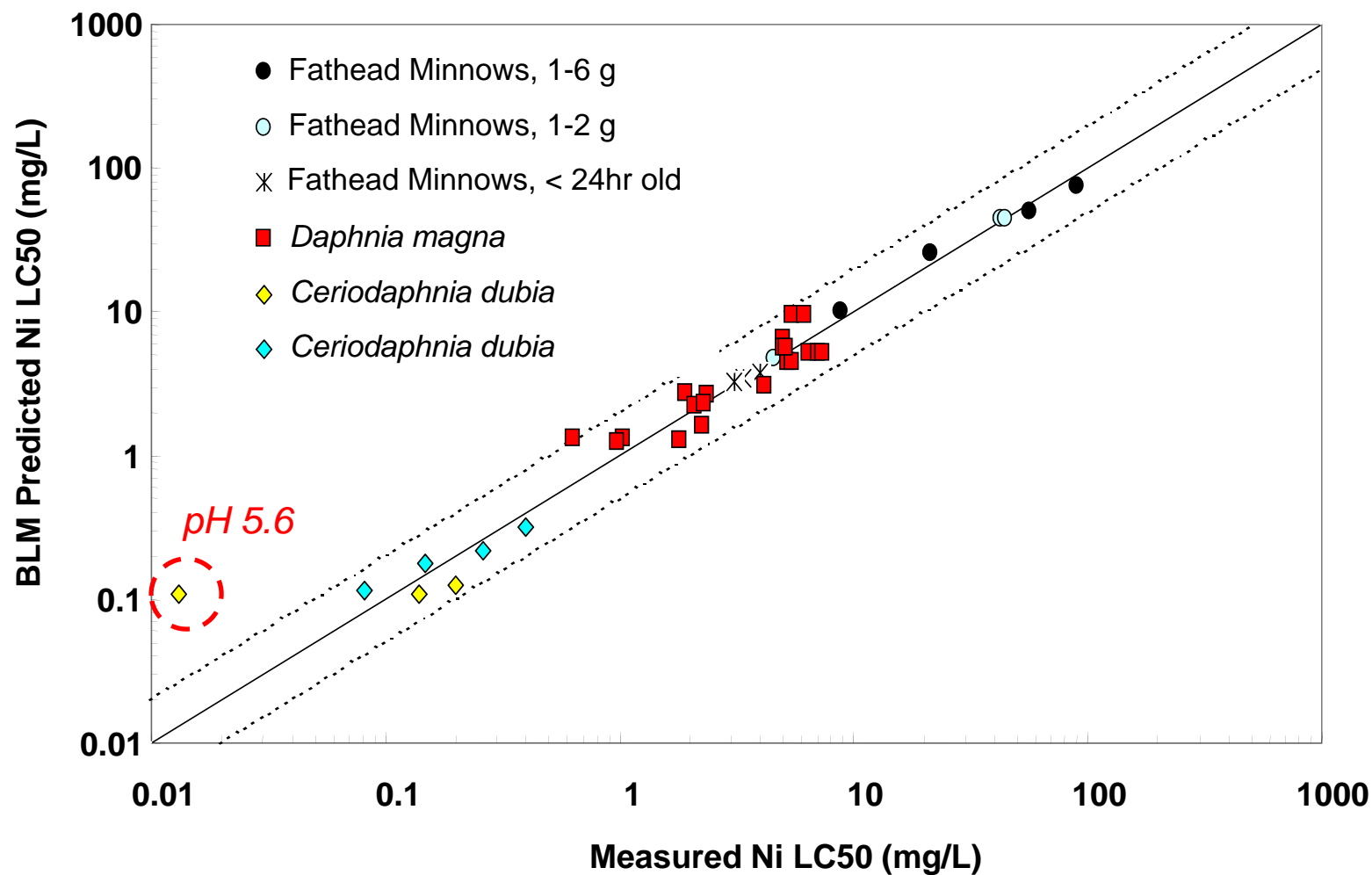
(Received 19 December 2002; Accepted 24 July 2003)

**Abstract**—This study evaluated acute and chronic nickel (Ni) toxicity to *Ceriodaphnia dubia* and *Hyaella azteca* with the objective of generating information for the development of a biotic ligand model for Ni. Testing with *C. dubia* was used to evaluate the effect of ambient hardness on Ni toxicity, whereas the larger *H. azteca* was used to derive lethal body burden information for Ni toxicity. As was expected, acute *C. dubia* median lethal concentrations (LC50s) for Ni increased with increasing water hardness. The 48-h LC50s were 81, 148, 261, and 400  $\mu\text{g/L}$  at hardnesses of 50, 113, 161, and 253  $\text{mg/L}$  (as  $\text{CaCO}_3$ ), respectively. *Ceriodaphnia dubia* was found to be significantly more sensitive in chronic exposures than other species tested (including other daphnids such as *Daphnia magna*); chronic toxicity was less dependent on hardness than was acute toxicity. Chronic 20% effective concentrations (EC20s) were estimated at <3.8, 4.7, 4.0, and 6.9  $\mu\text{g/L}$  at hardnesses of 50, 113, 161, and 253  $\text{mg/L}$ , respectively. Testing with *H. azteca* resulted in a 96-h LC50 of 3,045  $\mu\text{g/L}$  and a 14-d EC20 of 61  $\mu\text{g/L}$  at a hardness of 98  $\text{mg/L}$  (as  $\text{CaCO}_3$ ). Survival was more sensitive than was growth in the chronic study with *H. azteca*. The 20% lethal accumulation effect level based on measured Ni body burdens was 247  $\text{nmol/g}$  wet weight.

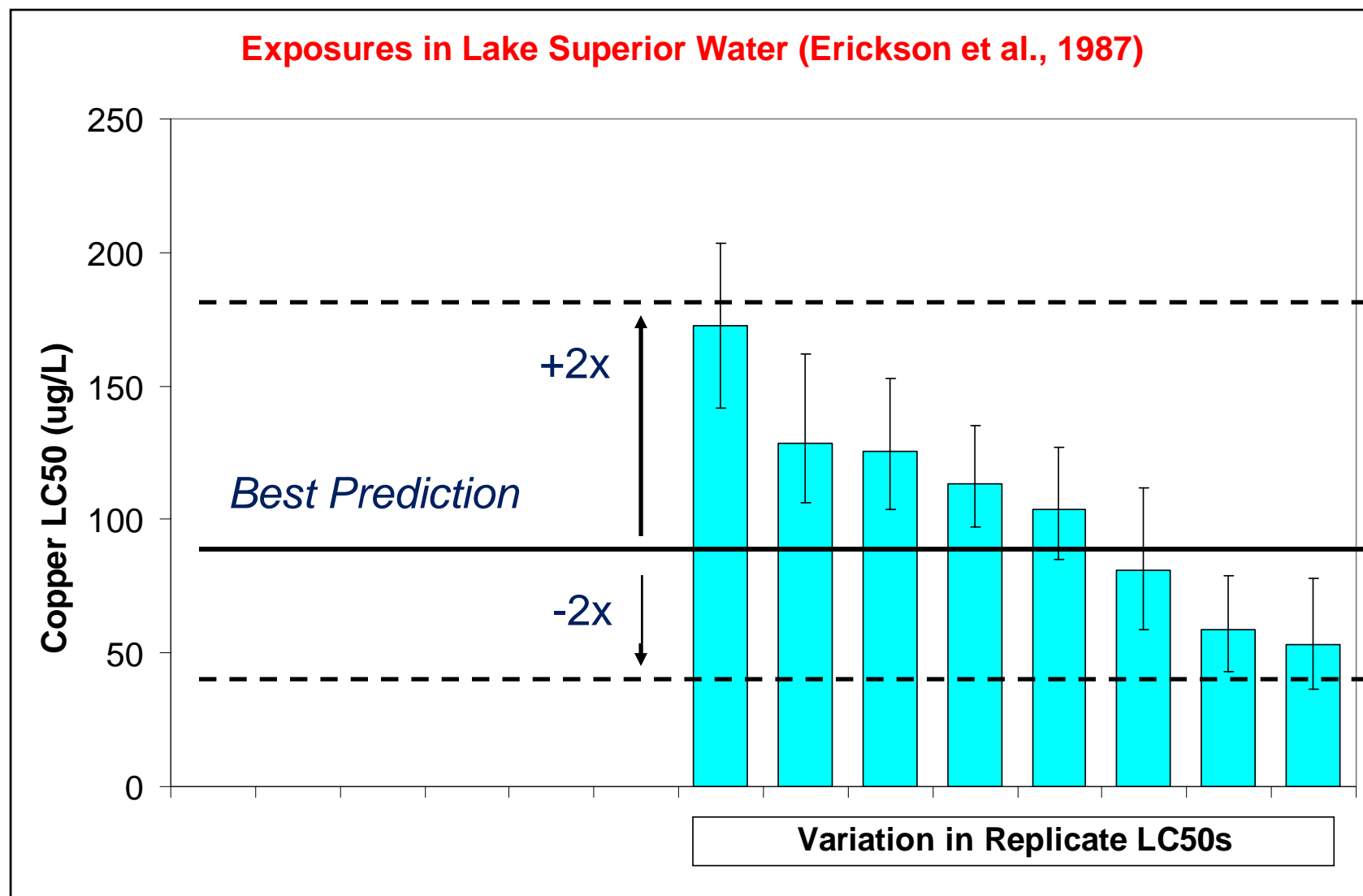
**Keywords**—Nickel Daphnids Amphipods Biotic ligand model



# Overall calibration results to fish and invertebrates



# Variability in Measured Cu LC50s

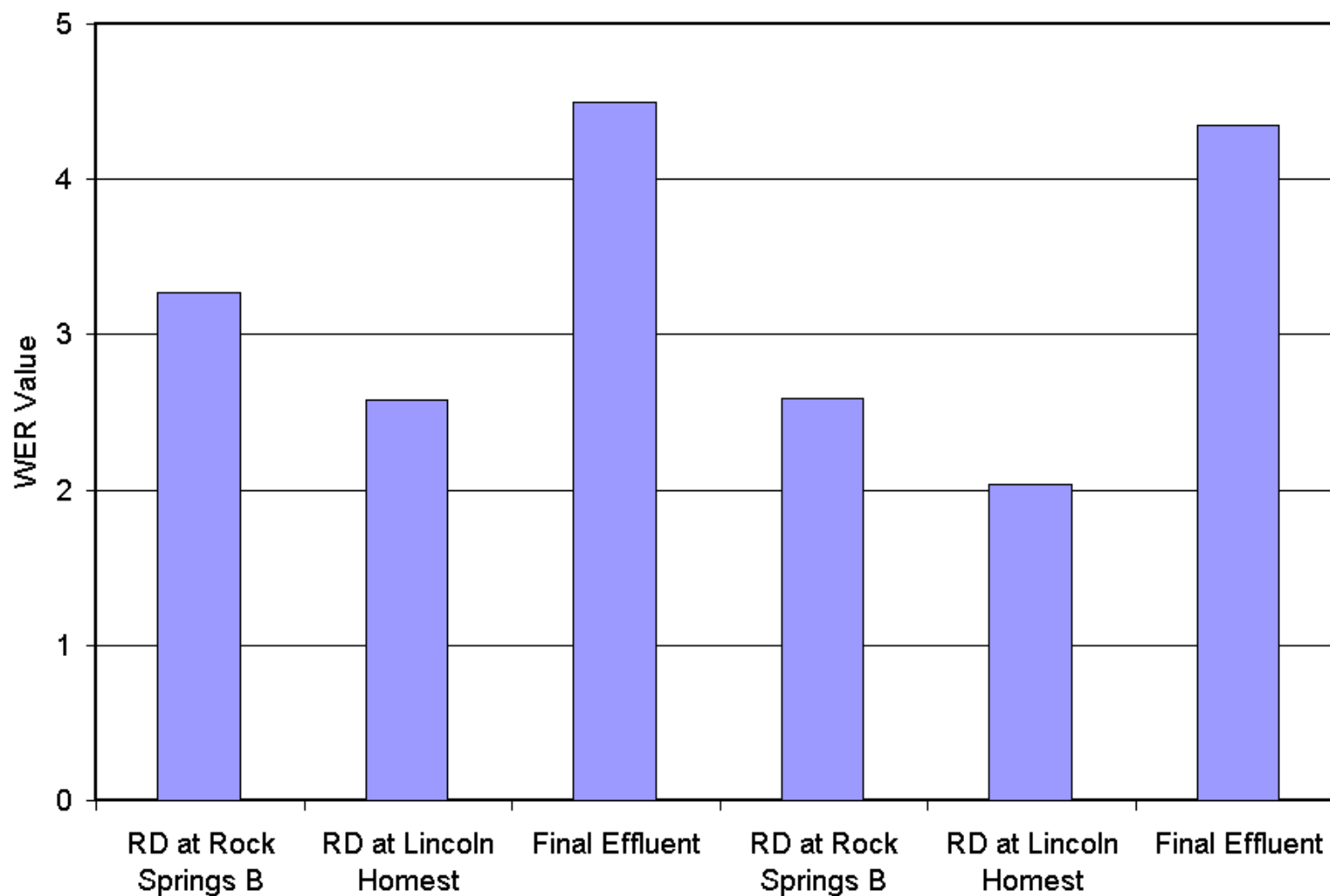


# Method to Calculate WER

- Use the BLM to estimate Ni toxicity to a sensitive aquatic organism suitable for use in a WER study (*Daphnia magna*)
- Site water will be characterized by the provided chemistry
- Reference water will be standard EPA recipe (very hard)
- $WER = (\text{Site Water LC50}) / (\text{Reference LC50})$

# Revised calculated WERs

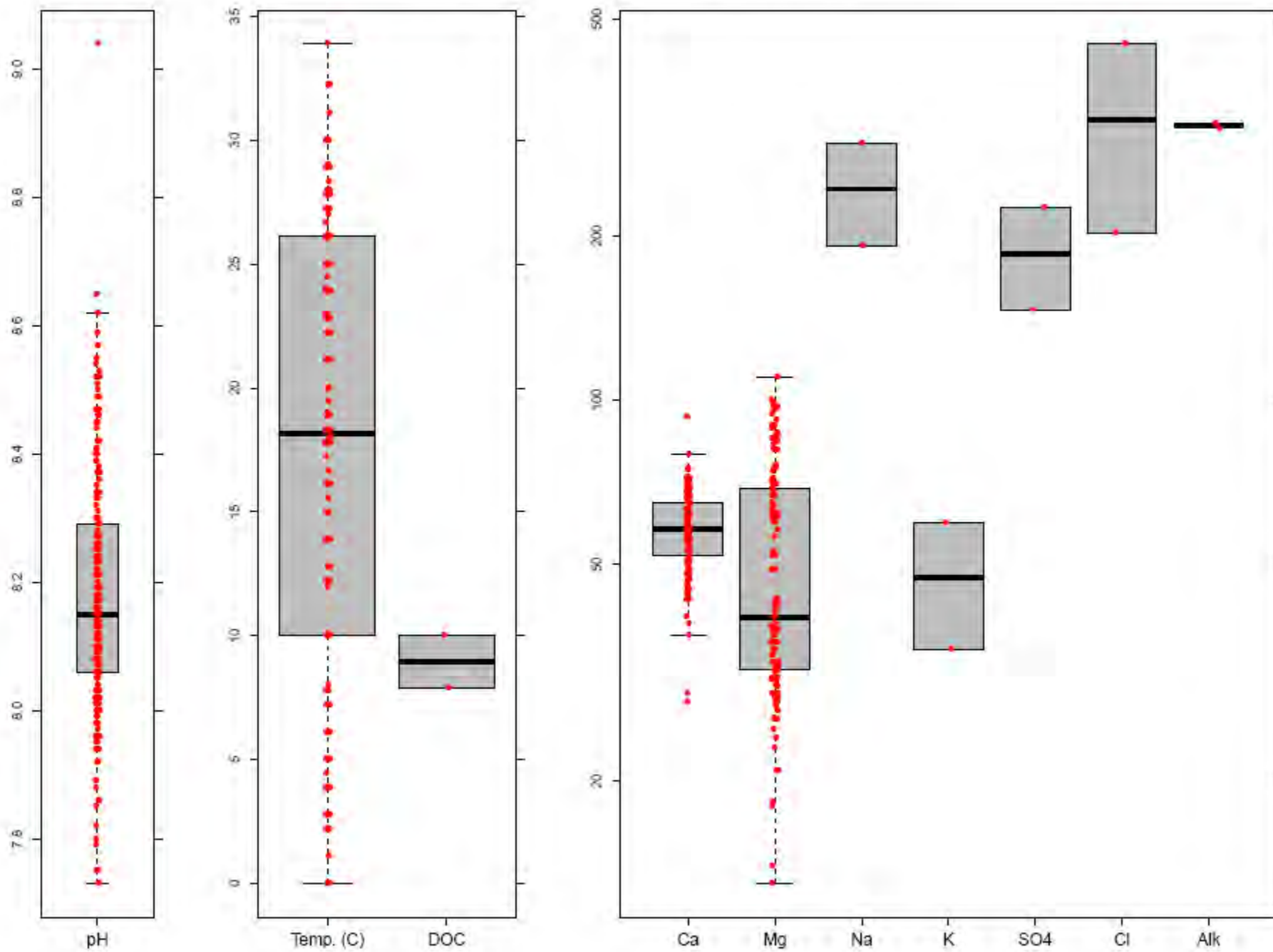
Range 2.0 to 4.3, Average 3.1, Downstream Avg 2.6



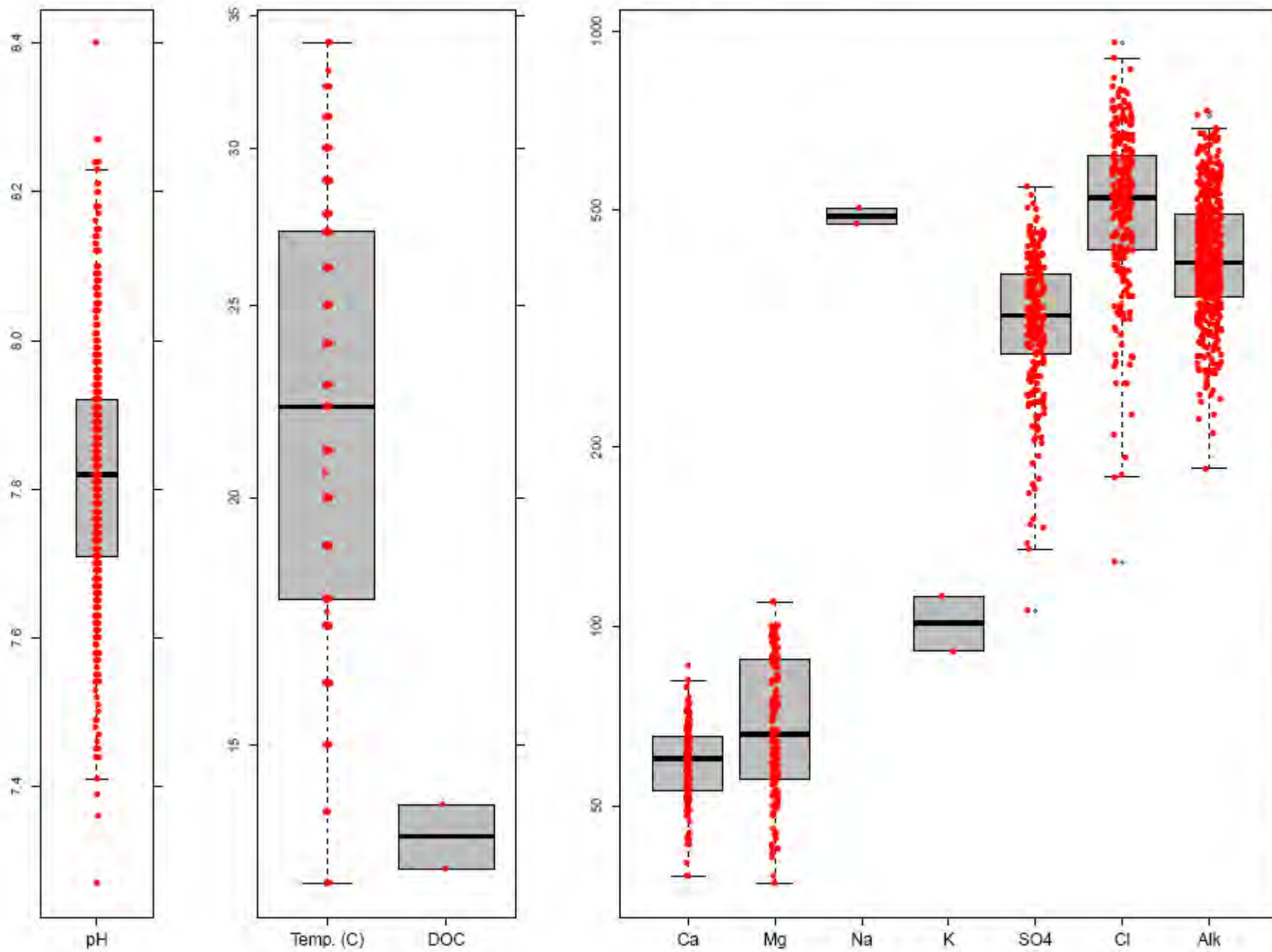
# Water Quality Variability

- Additional monitoring data for all BLM parameters were obtained
- These additional data provide insight in the range and variation of parameter values for BLM inputs
- Data do not necessarily represent coincident measurements in a given sample
- Can be used to estimate effects of chemical variability (due to seasonal or other factors) on model results

River: distribution of BLM input parameters



Effluents: distribution of BLM input parameters



# Sensitivity Analysis: Approach

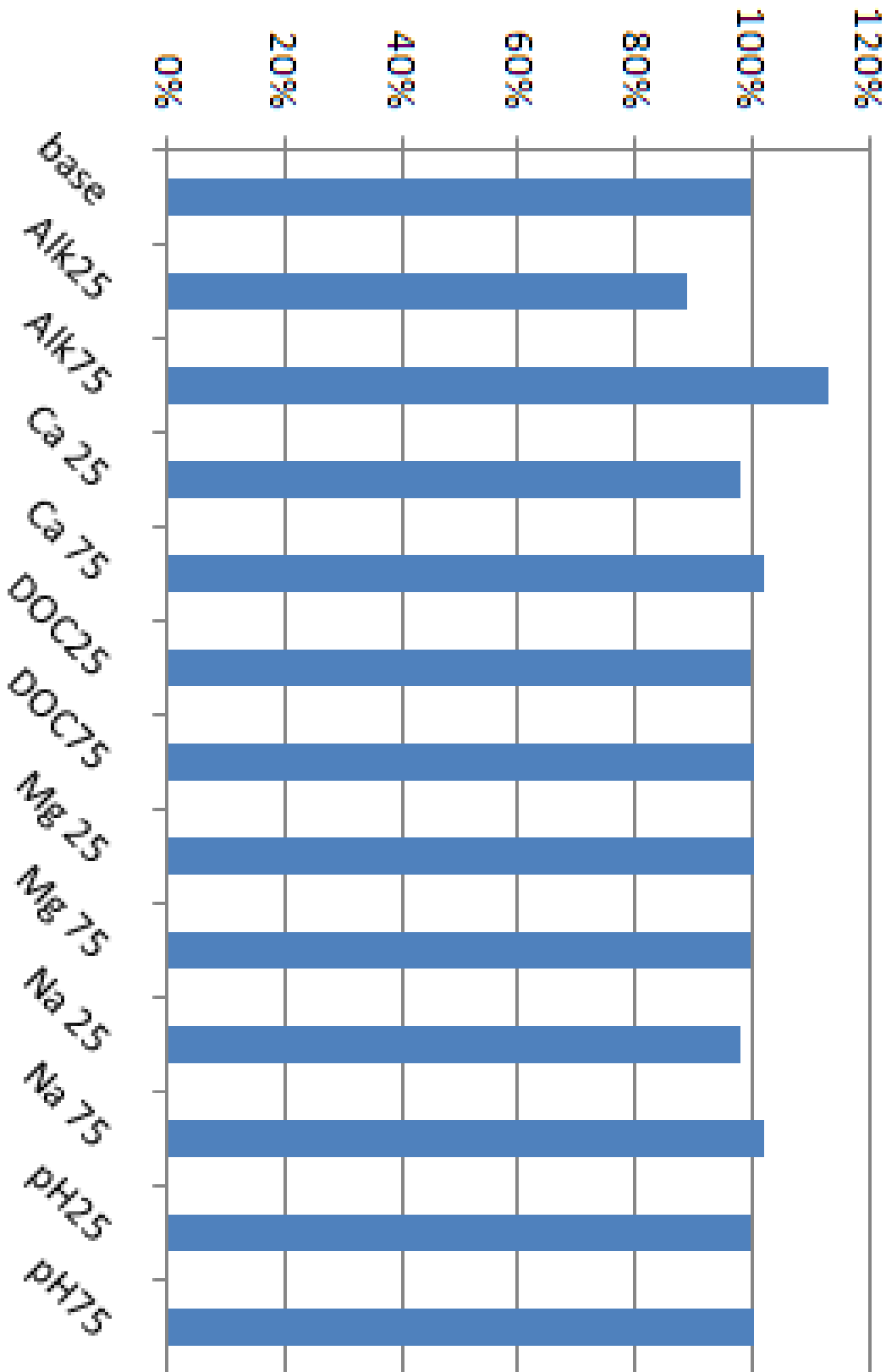
- For each input parameter, “base line” condition was defined as the median value
- For each parameter, a simulation was run using the 25<sup>th</sup> and 75<sup>th</sup> percentile value
- The effects of variation in that single parameter on model output was calculated as a simple ratio

$$\text{Toxicity (relative to base case)} = (\text{LC50}(\text{var})/\text{LC50}(\text{base})) * 100$$

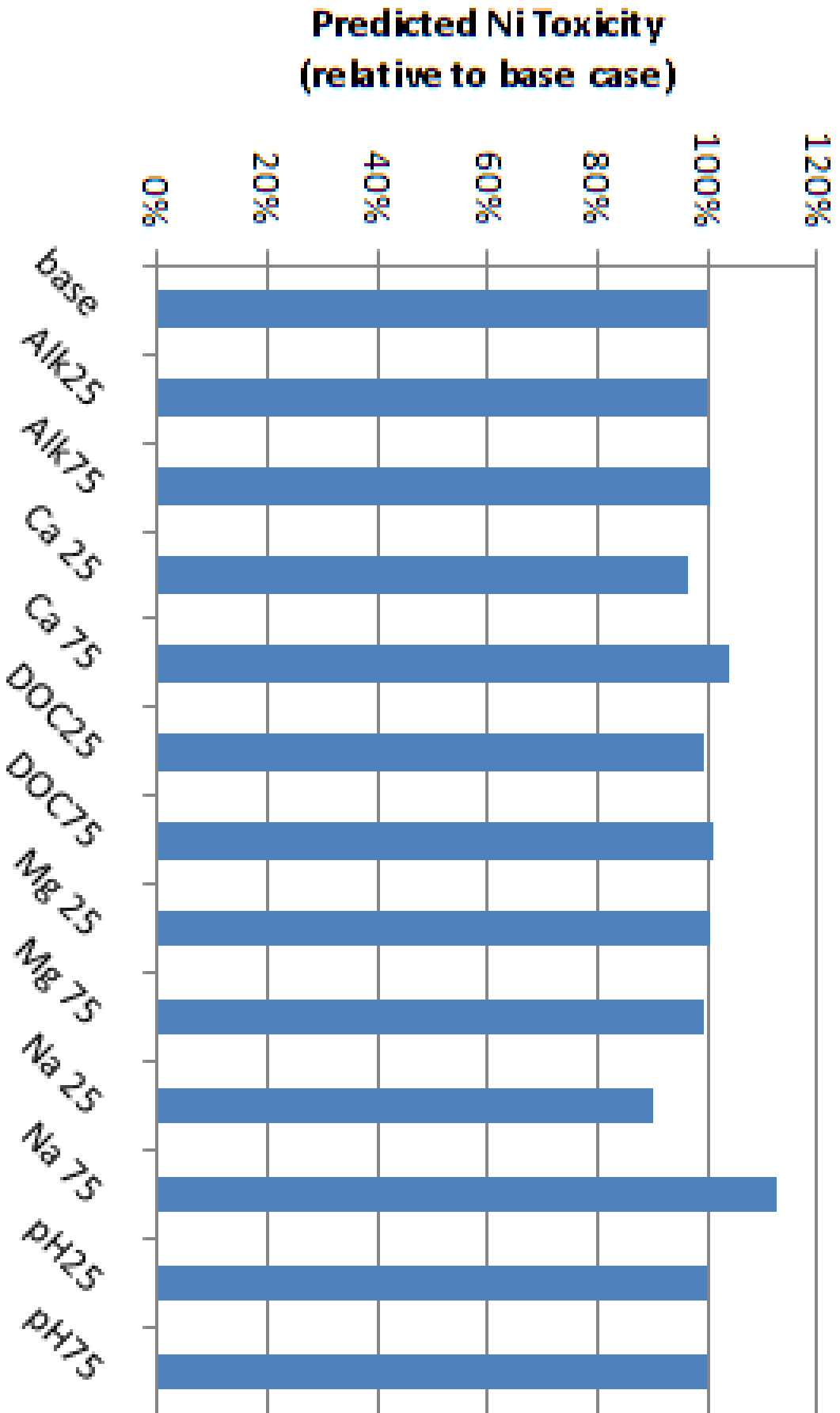


# Sensitivity Analysis: Results Effluent

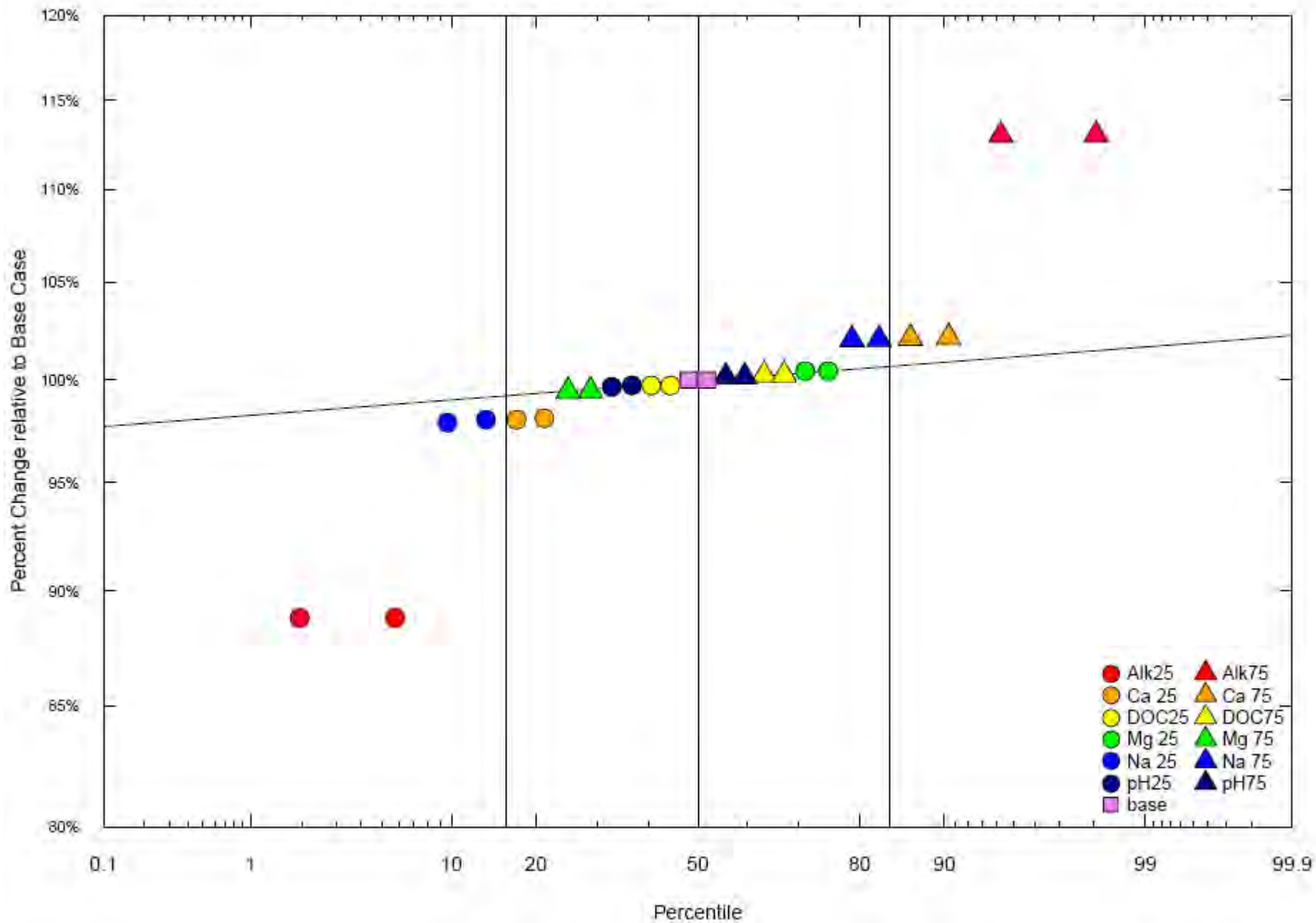
**Predicted Ni Toxicity  
(relative to base case)**



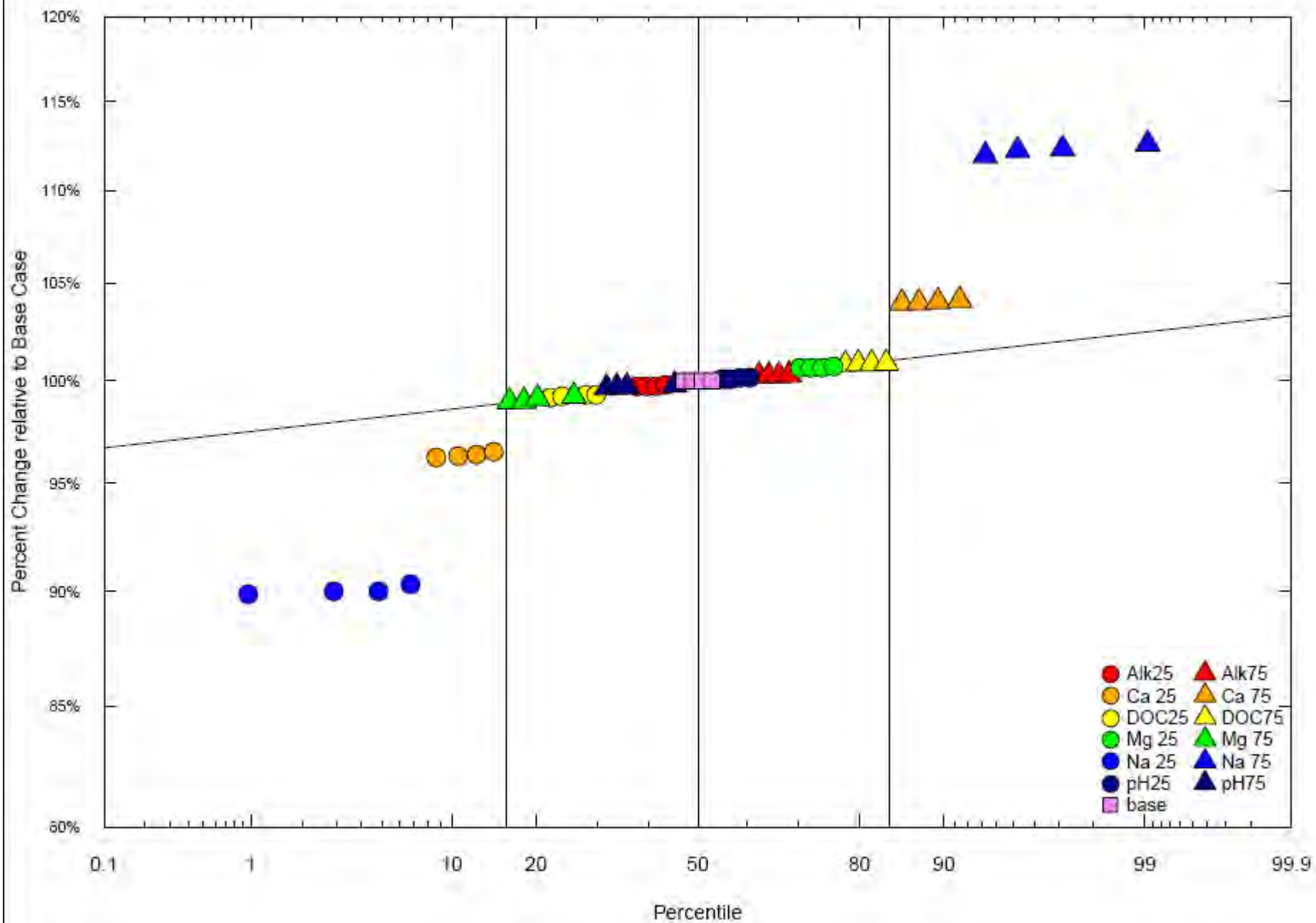
# Sensitivity Analysis: Results River



Percent change probability distribution for Effluent



Percent change probability distribution for River



# Parameter variability summary

- Extensive monitoring data used to characterize variability in input parameters
- Base case defined as the median for each parameter
- Comparison of BLM results at 25<sup>th</sup> and 75<sup>th</sup> percentiles for each individual parameter relative to base case shows chemical variability may result in  $\pm 15\%$
- This amount of variability is small, especially when comparison to variability in replicate toxicity tests

# Estimated WER

- The acute standard in IL  
 $CMC = e(0.8460[\ln(\text{hardness})] + 0.5173)$ 
  - At a hardness of 347,  $CMC = 218.5 \mu\text{g/L}$
  - Adjusted by WER,  $SSCMC = 564 \mu\text{g/L}$
- The chronic (geomean) standard in IL  
 $FCV = e(0.8460[\ln(\text{hardness})] - 2.286)$ 
  - At a hardness of 347,  $FCV = 14.3 \mu\text{g/L}$
  - Adjusted by WER,  $SSFCV = 37 \mu\text{g/L}$

# Conclusions

- Measured water chemistry gives comparable results to previous estimates
- BLM Calculated WER ranges from 2.0 to 4.3, and tends to be lower in downstream samples
- A WER adjusted criteria calculated only using downstream BLM predictions is somewhat lower than previously shown, but still considerably higher than the unadjusted acute and chronic criteria

Prepared for Proposed Site Specific Rule for Sanitary District of Decatur  
From 35 Ill. Adm. Code Section 302.208(e)

---

# **ESTIMATE OF THE BLM ADJUSTMENT TO THE NICKEL CRITERION FOR THE SANITARY DISTRICT OF DECATUR, ILLINOIS**

Prepared by

Robert Santore



January 16, 2014



## **I. INTRODUCTION**

This report was prepared in support of the Sanitary District of Decatur's ("District") Petition to the Illinois Pollution Control Board ("Board") seeking a Site Specific Rule to establish an alternative water quality standard ("WQS") for Nickel from the point of its discharge into the Sangamon River from its Main Sewage Treatment Plant ("Main Plant") to the point of the confluence of the Sangamon River with the South Fork of the Sangamon River near Riverton, Illinois. The purpose of this report is to present the calculations, comparisons, and findings acquired from using the federally approved Biotic Ligand Model ("BLM") to adjust the Nickel WQS such that it considers local conditions found in that segment of the Sangamon River.

Adjustment of the WQS for metals in consideration of the local chemical conditions has frequently been shown to be appropriate at sites across the United States, since WQSs are based on water quality criteria ("WQC") that are defined using a traditional methodology that does not consider many of the factors that are known to affect metal toxicity to aquatic organisms. For example, the WQC for several metals (including Silver ("Ag"), Cadmium ("Cd"), Chromium (III) ("Cr(III)"), Lead ("Pb"), Nickel ("Ni"), and Zinc ("Zn"), as well as Copper ("Cu") prior to development of the BLM) are dependent on the hardness of the local water. The term "hardness" refers to the mineral content of the water and is primarily associated with the combined concentration of Calcium ("Ca") and Magnesium ("Mg"). Hardness is one of several key water quality constituents that have been shown to affect metal bioavailability and toxicity. The United States Environmental Protection Agency's ("US EPA") approach for deriving metals WQC as hardness-dependent relationships has considered how variation in toxic response may differ in areas that naturally have either very hard or very soft water.

However, factors other than hardness have been shown to affect metal bioavailability, and in particular variation in pH, Alkalinity ("Alk"), and the presence of natural organic matter ("NOM") have all been shown to be as important, or even more important, than hardness in determining metal toxicity (Erickson, et al., 1996). These factors may increase or decrease the toxicity of metals. The dependence of metal toxicity on local chemical factors is referred to as the "bioavailability" of the metal to aquatic organisms. Since these bioavailability factors are not considered by WQC approaches that only consider hardness, the WQC may be more or less protective than needed for a specific receiving water. This issue has long been recognized by US EPA and, in response, US EPA has developed procedures for derivation of site specific adjustments to WQC (Carlson, et al. 1984; US EPA, 1992, 1994a). In particular, the Water Effect Ratio ("WER") approach is intended to account for local bioavailability factors that can affect metal toxicity (US EPA, 1994b). The site specific adjustment to a WQC provided by a WER is intended to correct for deficiencies in the WQC derivation process and to reduce the degree to which a WQC is over-protective or under-protective for a given location.

## II. BACKGROUND ON NICKEL BLM

Although the WER has been in use for decades, it requires toxicity testing with multiple aquatic organisms in multiple samples. Costs and time required to accommodate WER testing can be significant. As an alternative, the BLM is a computational approach that can simulate the effects of water chemistry on metal toxicity, and on the physiological response of aquatic organisms to metals (Di Toro, et al, 2001; Santore, et al, 2001). The BLM provides information that is similar to the WER, but does so with much less cost and time required. The BLM is a mechanistic approach, not an empirical approach like the hardness equation, and it considers effects from numerous chemical factors such as pH, the presence of NOM, Alkalinity, and major ions (including cations that contribute to hardness). The BLM considers how these factors affect either metal chemistry or organism physiology to determine metal bioavailability (Figure 1).

The BLM has been adopted by US EPA as a replacement for the hardness equation in the most recently updated metals criteria (US EPA, 2007). The use of the BLM provides similar benefits as the WER, and for criteria based on the BLM, the use of the WER is no longer required. For metals (such as Nickel) where US EPA has not adopted a BLM-based procedure for replacement of the hardness equation, the BLM can be used in a manner similar to the WER to modify the hardness equation based WQC. Use of the BLM to derive a site specific WQC provides the same level of protection as intended by US EPA guidelines (Stephan, et al, 1985). To the extent that a BLM derived site specific WQC is different from the national ambient WQC, those differences reflect how local factors which are not considered by the hardness-equation may change metal bioavailability and toxicity.

The BLM can be used to determine modifications to chemistry of receiving water using a procedure that is analogous to the WER. The WER compares the toxicity of Nickel or other toxicant in receiving water to that in reference water. The reference water is intended to represent the conditions comparable to those used to develop the toxicity database in which the acute and chronic WQC were developed. The WER is then simply the ratio of the measured toxic endpoint in the receiving water to that in the reference water. If multiple receiving water and reference water samples are used to generate the WER, the WER is determined for each pair of samples, and then an overall WER is usually determined as the geometric mean. The reference water chemistry must meet WER guidelines (US EPA, 1994b), and US EPA has provided synthetic recipes suitable for generating reference water samples with various hardness concentrations. These recipes can be incorporated into the BLM application to predict toxicity endpoints for suitable reference water that can be used in a WER-type analysis.

06/30/2014 - \* \* \* R2014-024 \* \* \*

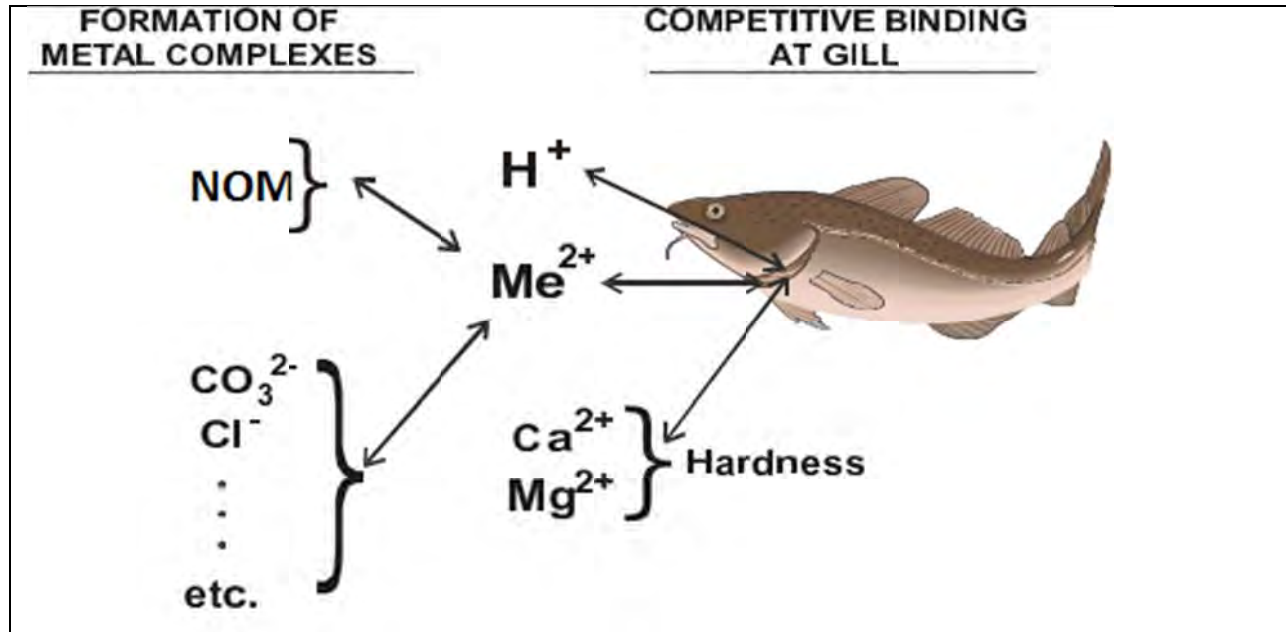


Figure 1. Conceptual model of the chemical and physiological processes represented in the BLM. Water chemistry, including inorganic complexes and binding by NOM, can affect the chemical speciation and reactivity of a metal (i.e.,  $\text{Me}^{2+}$ ). The accumulation of metal on biological surfaces, such as gill membranes, is related to the chemical reactivity of the metal as well as other factors such as pH and competitive binding of cations. The BLM is a general framework that has been applied to acute and chronic responses of numerous metals including Aluminum (“Al”), Ag, Cd, Cobalt (“Co”), Cu, Ni, Pb, and Zn.

### III. BLM RESULTS WITH MEASURED WATER QUALITY

#### A. Overall Calibration Results to Fish and Invertebrates

The BLM is a generalized mechanistic approach that has been applied to a number of different metals including Nickel. Development efforts for Nickel focused on explaining available toxicity data for sensitive aquatic invertebrates and fish in a project sponsored by the Water Environment Research Foundation (“WERF”) (WERF, 2003). The project for WERF included a detailed review of the chemical speciation of Nickel in freshwaters, analysis of Nickel accumulation in aquatic organisms, and a summary of important bioavailability factors, including pH, Alkalinity, hardness, and the presence of NOM. The performance of the Nickel BLM was quite good, with excellent agreement between predicted and measured toxicity over a range of several orders of magnitude (Figure 2). Nearly all of the predicted toxicity values are within a factor of two of measured values.

Agreement with a factor of two of a given measured toxicity value has been shown to be about the degree to which replicate measurements agree with a mean value. Replicate toxicity tests used to determine replicate LC50 values for the same organism in the same water frequently does not produce exactly the same result. For example, replicate copper toxicity measurements,

06/30/2014 - \* \* \* R2014-024 \* \* \*

expressed as the median lethal concentration to 50% of the population (LC50), made to the same species of fish in water samples from Lake Superior tend to fall in  $\pm 2x$  envelope around a central mean (Figure 3; data are from Erickson et al., 1996). If replicate measurements agree with a central mean value no better than  $\pm 2x$ , then comparison of predicted toxicity values with measured values with a factor of  $\pm 2x$  would be the best that could be expected. Hence, predicted values such as those shown in Figure 2 are often shown within a  $\pm 2x$  envelope around the line of perfect agreement, and predicted values that fall within this envelope show excellent agreement with measured values.

The strength of the predictive ability of the BLM lies in the mechanistic and generalized nature of the model. Although the model simulates a complex set of chemical reactions and biological accumulation processes, these processes are characterized as generalized reactions based on thermodynamics. The model can therefore predict accumulation in aquatic organisms without recalibration of any of the model parameters that describe chemical speciation, or organism accumulation. Application of the same model and same model parameters are used to predict effects to diverse aquatic organisms including fish and invertebrates. The consistency of this approach is evidence of the mechanistic and generally applicable nature of this analysis. The only parameter that varies from one organism to another is the concentration of accumulated metal associated with toxicity (Santore, et al, 2001). The resulting model is capable of simulating Nickel toxicity to a range of organisms in a wide range of chemical conditions (Figure 2).

06/30/2014 - \* \* \* R2014-024 \* \* \*

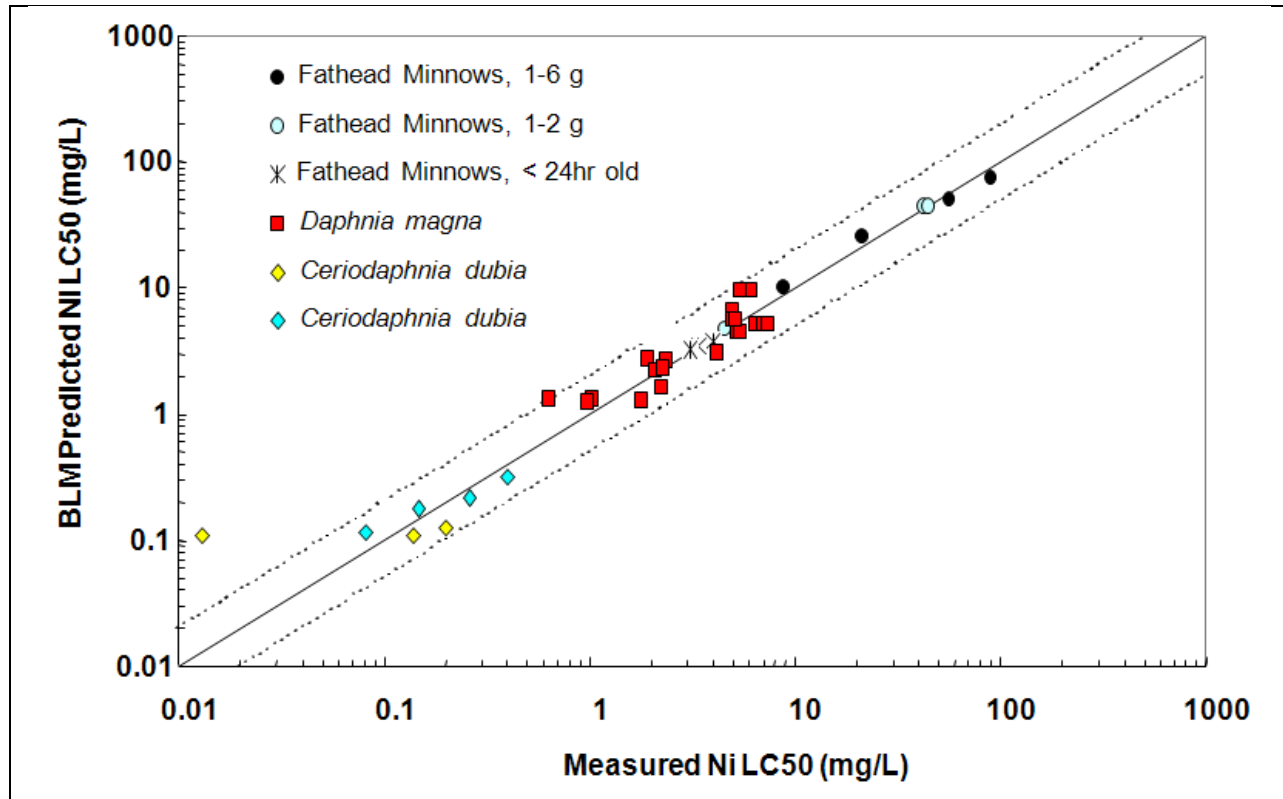


Figure 2. Comparison of the calibrated Nickel BLM to sensitive freshwater aquatic invertebrates and fish. Measured toxicity, as the lethal concentration to 50% of the test organisms, is shown on the horizontal axis. Predicted toxicity is shown on the vertical axis. The diagonal solid black line shows perfect agreement between measured and predicted values, and the dashed black lines show a region of  $\pm$  factor of 2x from perfect agreement. The  $\pm$  factor of 2x is intended to show agreement between measured and predicted values that comparable to the expected agreement between replicate measurements.

06/30/2014 - \* \* \* R2014-024 \* \* \*

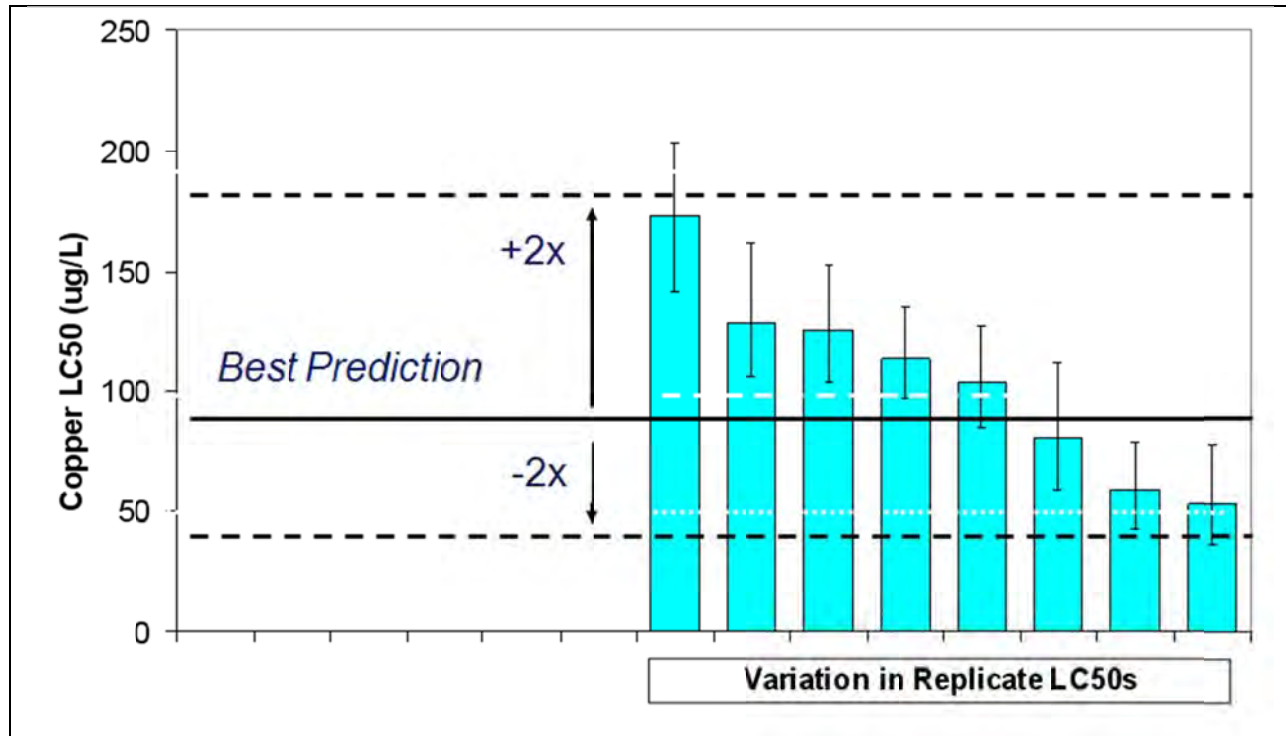


Figure 3. Variation in replicate measurements of LC50 of copper to fathead minnow in Lake Superior water tends to fall in an envelope of plus or minus 2 times the geometric mean value (date from Erickson et al., 1996). The dark solid line labeled "Best Prediction" is shown at the geometric mean of the measured values. The dashed lines correspond to an envelope showing plus or minus a factor of two. Since all of these measured values are from water samples with the same chemistry, the BLM would predict the same LC50 in every case.

06/30/2014 - \* \* \* R2014-024 \* \* \*

#### IV. CALCULATED WER WITH PREDICTED TOXICITY TO *DAPHNIA MAGNA*

As discussed in Section II of this report, the BLM for Nickel can be used to calculate a site specific WQC by using the model to calculate a WER for the receiving water downstream of the Main Plant. Samples were collected at two locations downstream of the Main Plant discharge, and chemical analyses for BLM input parameters were measured on these samples. Similar analyses were made on samples taken from the Main Plant effluent, although these were not used in the WER analysis. Measured chemical parameters used as input parameters to the Nickel BLM are shown in Table 1.

The BLM for Nickel was run with these input data to determine Nickel toxicity to *D. magna*, which is a sensitive invertebrate recommended for use in WER testing for Nickel (USEPA, 1994b, Appendix I). For calculation of WER values, the predicted toxicity in these site waters was compared with toxicity in a reference water sample. According to the WER guidance document, suitable reference water must have a hardness concentration close to, but not in excess of, the measured hardness in the site water (US EPA, 1994b). The US EPA's recipe for "very hard" water with a hardness of 317 mg/L as Calcium Carbonate ("CaCO<sub>3</sub>"), compared with hardness in the site water of 347, would be a suitable choice for use as a reference water for WER testing at the site. Calculated LC50 values for site and reference water are shown in Table 2.

06/30/2014 - \* \* \* R2014-024 \* \* \*

Table 1. Input chemistry used for BLM analyses. For site waters, Sangamon River samples collected at the Rock Springs Trail bridge approximately one-half mile downstream (RD at Rock Springs) and at the South Lincoln Memorial Parkway bridge approximately six miles downstream (RD at Lincoln) were used to characterize the chemistry of the receiving water downstream of the plant. The presence of NOM was characterized by the dissolved organic carbon (“DOC”) concentration. For calculation of WER, the US EPA’s ”very hard” water recipe was used as a reference sample. Variation of an assumed DOC in the reference water sample from 0.5 to 2.0 mg C/L was included in the BLM analysis.

Sample Description		Temp °C	pH	DOC mg C/L	Ca	Mg	Na	K	SO4	Cl	Alk
									----- mg / L -----		
RD at Rock Springs	8/26/2010	23	8.00	12	56	53	396	86	298	446	365
RD at Rock Springs	9/9/2010	21	8.09	10	64	48	286	53	214	304	341
RD at Lincoln	8/26/2010	25	8.00	10	58	46	296	60	225	450	321
RD at Lincoln	9/9/2010	21	8.10	7.9	65	43	192	35	146	202	315
Final Effluent	8/26/2010	30	8.09	13	56	62	504	112	374	558	400
Final Effluent	9/9/2010	28	7.90	14	62	62	474	91	328	477	399
US EPA Very Hard	DOC=0.5	20	8.20	0.5	47	48	105	8	304	8	229
US EPA Very Hard	DOC=1.0	20	8.20	1	47	48	105	8	304	8	229
US EPA Very Hard	DOC=2.0	20	8.20	2	47	48	105	8	304	8	229



06/30/2014 - \* \* \* R2014-024 \* \* \*

Table 2. Predicted toxicity to *D. magna* by the Nickel BLM in site and reference water samples used in WER analysis. For calculation of WER values, the average LC50 determined in site water was divided by the average LC50 in the reference water. The US EPA's "very hard" recipe for synthetic water was chosen as the reference water due to the good correspondence between the hardness in this recipe and at the site.

Sample Description		Ni LC50 mg/L	Average Ni LC50 mg/L	Average WER
RD at Rock Springs	8/26/2010	32.38	28.89	2.92
RD at Rock Springs	9/9/2010	25.61		
RD at Lincoln	8/26/2010	25.55	22.84	2.31
RD at Lincoln	9/9/2010	20.13		
Final Effluent	8/26/2010	44.52	43.78	4.42
Final Effluent	9/9/2010	43.04		
US EPA Very Hard	DOC=0.5	9.82	9.90	
US EPA Very Hard	DOC=1.0	9.88		
US EPA Very Hard	DOC=2.0	10.00		

Site water was characterized by performing two separate sampling events at both Rock Springs B and Lincoln Homestead. The BLM calculated LC50 values to *D. magna* in site-waters downstream of the Main Plant ranged from 22.84 mg/L to 28.89 mg/L (Table 2). For comparison, the calculated LC50 for reference water based on the US EPA's "very hard" water recipe was 9.9 mg/L. The WER values for each sampling location, calculated by dividing site water LC50 by the reference water LC50, correspond to 2.31 and 2.92 for Rock Springs B and Lincoln Homestead. Since these values are similar, an overall WER for the site can be determined by averaging to obtain an overall WER for the site of 2.62.

Predicted toxicity in the Final Effluent and the resulting WER value is also shown for comparison in Table 2, but these values were not averaged into the overall WER for the site. The predicted average LC50 in effluent samples was 43.78 mg/L, which is considerably higher than in downstream receiving water samples. The chemistry for the effluent shown in Table 1 indicates that effluent samples had higher concentrations of cations, such as Ca, Mg, and Sodium ("Na"), as well as a higher concentration of NOM (measured as DOC). All of these factors would tend to further mitigate against Nickel toxicity to aquatic organisms, which is why the predicted LC50 in effluent samples is higher. As a result, Nickel toxicity would be lower in any areas that are poorly mixed downstream of the discharge, and the resulting WER would be protective for these areas as well.

## V. SENSITIVITY TO VARIATION IN WATER CHEMISTRY

Since relatively few samples were used in the BLM analysis summarized in Tables 1 and 2, an additional analysis was conducted to see what effect natural variation in downstream water chemistry would have on the predicted toxicity. Additional monitoring data were used to characterize variation in measured chemistry corresponding to BLM input parameters. Monitoring data describing the variability in downstream chemistry was collected by the District, and combined with monitoring data for the Sangamon River collected by Eastern Illinois University. Samples collected for these monitoring studies were obtained at a number of different stations downstream of the Main Plant, including Lincoln, Rock Springs, and Wyckles Bridge, as well as unnamed stations 100 yards and 600 yards downstream. Variability in measured chemistry in the pooled data from these sampling stations includes both spatial and temporal variation. From these available data, the 10<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentiles were estimated for key water quality parameters that are known to affect Nickel bioavailability, including pH, DOC, Ca, Mg, Na, and Alkalinity (Table 3). A set of base case conditions was established as the median value for all parameters. Variation in Potassium (“K”), Sulfate (“SO4”), and Chlorine (“Cl”) was not considered since these parameters are not important in determining the bioavailability of nickel.

---

Table 3. Variation in water quality parameters that affect Nickel bioavailability was characterized as the 10<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentile estimated from a dataset of pooled measurements are stations downstream of the Decatur Plant. The values for the base case were based on median values from the same dataset.

Test	Temp. C	pH SU	DOC mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO4 mg/L	Cl mg/L	Alk mg/L
<i>base</i>	17.78	8.14	9.99	37.1	44.7	244.00	47.4	185.5	326.0	279.00
<i>10th</i>		7.96	3.7	25.4	15.8	202.4				151.2
<i>25th</i>		8.03	6.4	30.5	20.1	218.0				223.0
<i>75th</i>		8.29	14.8	73.6	64.9	270.0				321.0
<i>90th</i>		8.47	28.2	84.3	74.3	285.6				451.2

These data correspond to pre-existing monitoring studies and were not specifically collected for BLM analyses. Consequently, not all BLM parameters were measured in every sample. For the purposes of conducting a sensitivity analyses, these data are suitable for showing the expected downstream variation in individual parameters. Available data are plotted in Figure 4 for river samples and Figure 5 for effluent samples.

06/30/2014 - \* \* \* R2014-024 \* \* \*

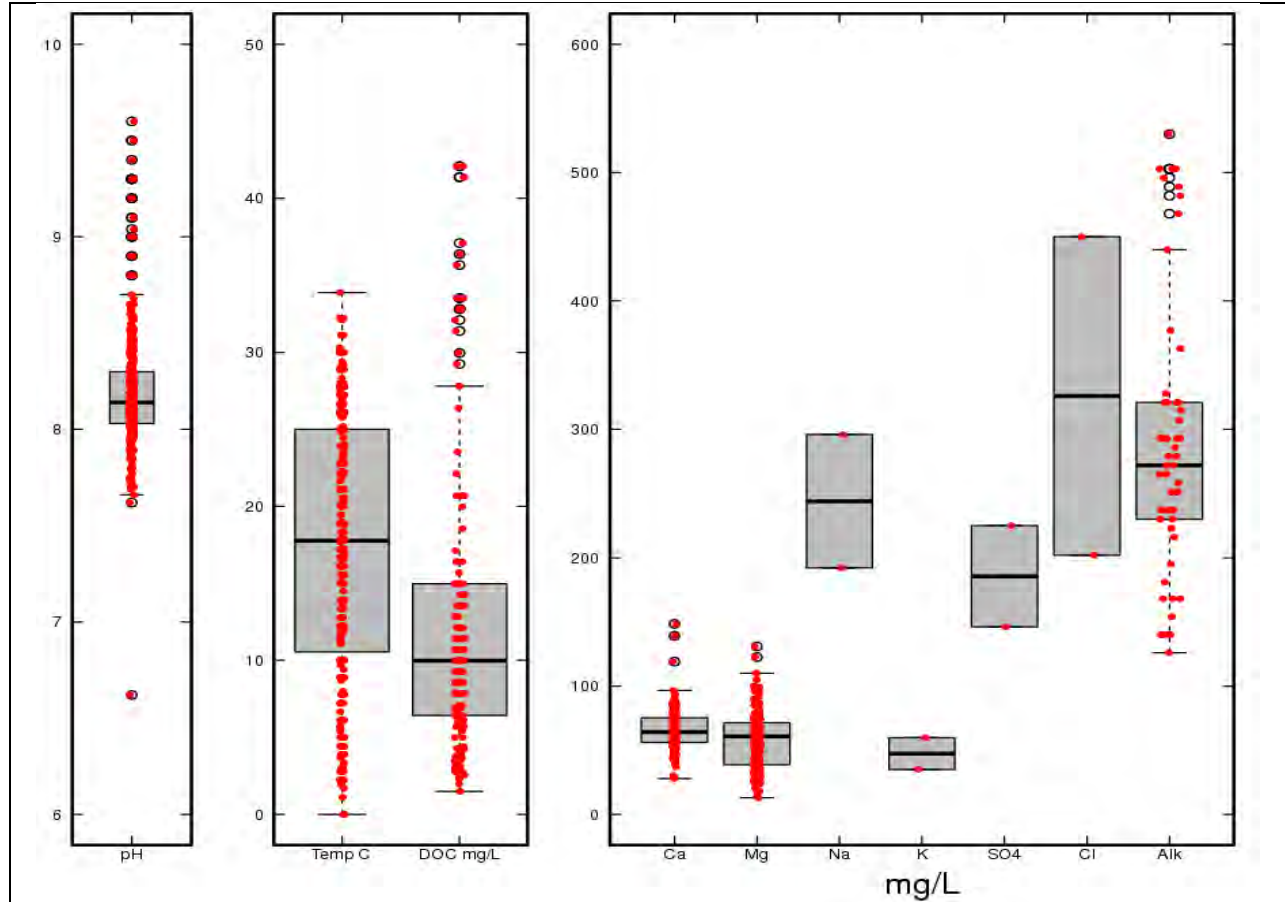


Figure 4. Box and whisker plots showing distributions of measured values for BLM input parameters in river samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO<sub>4</sub>, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25<sup>th</sup> percentile, the upper edge of the box represents the 75<sup>th</sup> percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

The distribution of values for each parameter are shown as box and whisker diagrams constructed so that the lower edge of the box represents the 25<sup>th</sup> percentile, the upper edge of the box represents the 75<sup>th</sup> percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Median values are shown as the solid black horizontal line in the middle of each box. Individual observations are shown as small red circles. For river samples, there was a large amount of data characterizing pH, Alkalinity, DOC, and hardness cations (Ca and Mg), which are the bioavailability factors that are the most important for determining Nickel toxicity (Figure 4). There were relatively few samples characterizing K, and SO<sub>4</sub>, but these parameters have little to no effect on Nickel toxicity and do not need to be considered in the uncertainty analysis. There were also relatively few observations for Na, but the estimated variation in Na concentrations is similar to that seen for Ca and Mg and is, therefore, likely to be a reasonable characterization of variation in downstream chemistry. For effluent samples there

06/30/2014 - \* \* \* R2014-024 \* \* \*

were many more measurements of anion concentrations (Figure 5), and in comparison with river samples the effluents tended to have lower pH values and higher DOC and ion concentrations. The variation in pH, DOC, and ion concentrations show in these two datasets are consistent with the values seen in detailed sample analyses reported in Table 1.

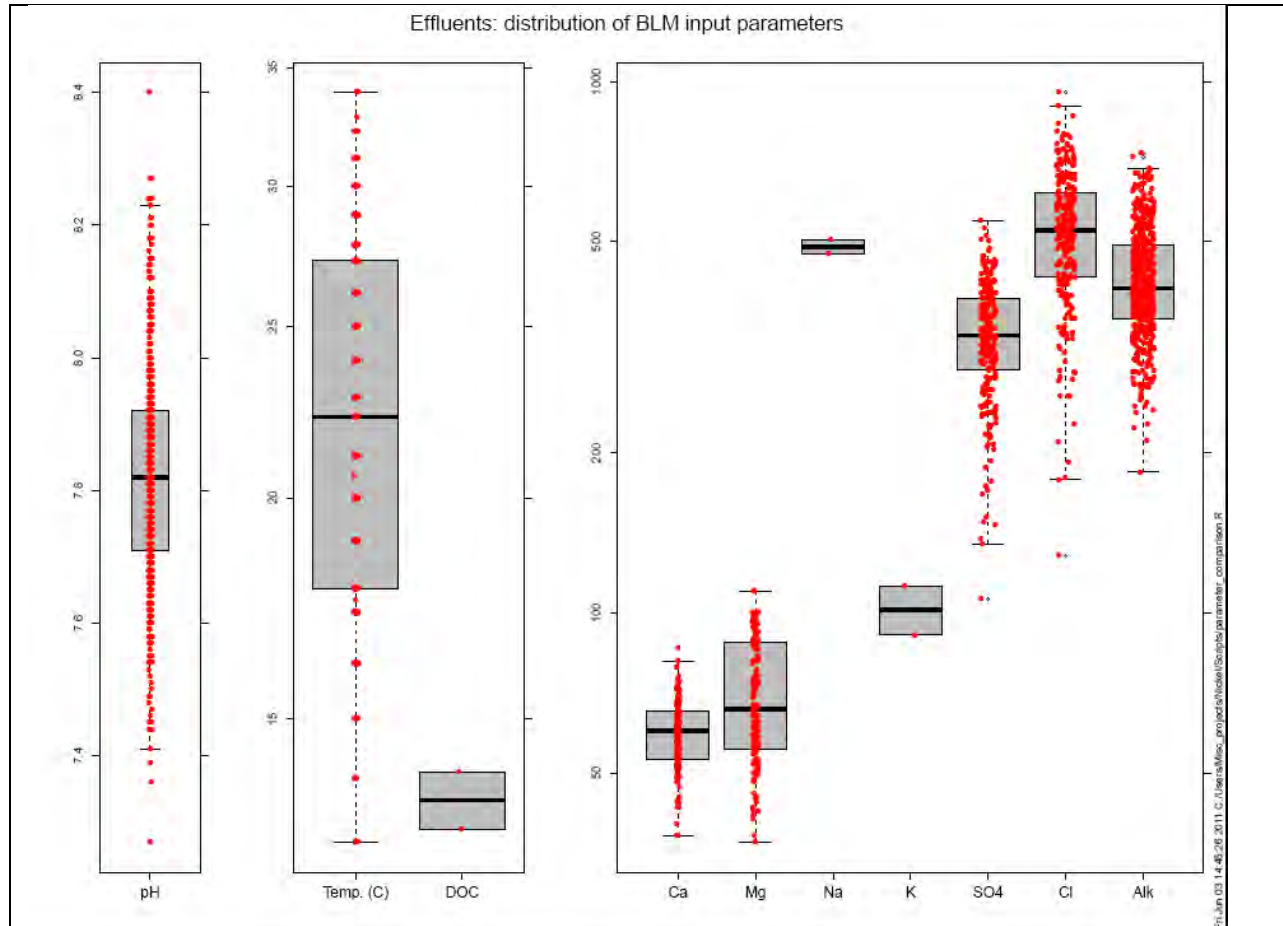


Figure 5. Box and whisker plots showing distributions of measured values for BLM input parameters in effluent samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO<sub>4</sub>, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25<sup>th</sup> percentile, the upper edge of the box represents the 75<sup>th</sup> percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

06/30/2014 - \* \* \* R2014-024 \* \* \*

Variability in BLM input parameters was used in a sensitivity analysis to determine the degree to which predicted toxicity may be expected to change over time. The model was first run for a base case that used median values for all parameters shown in Figure 4 and Table 3.

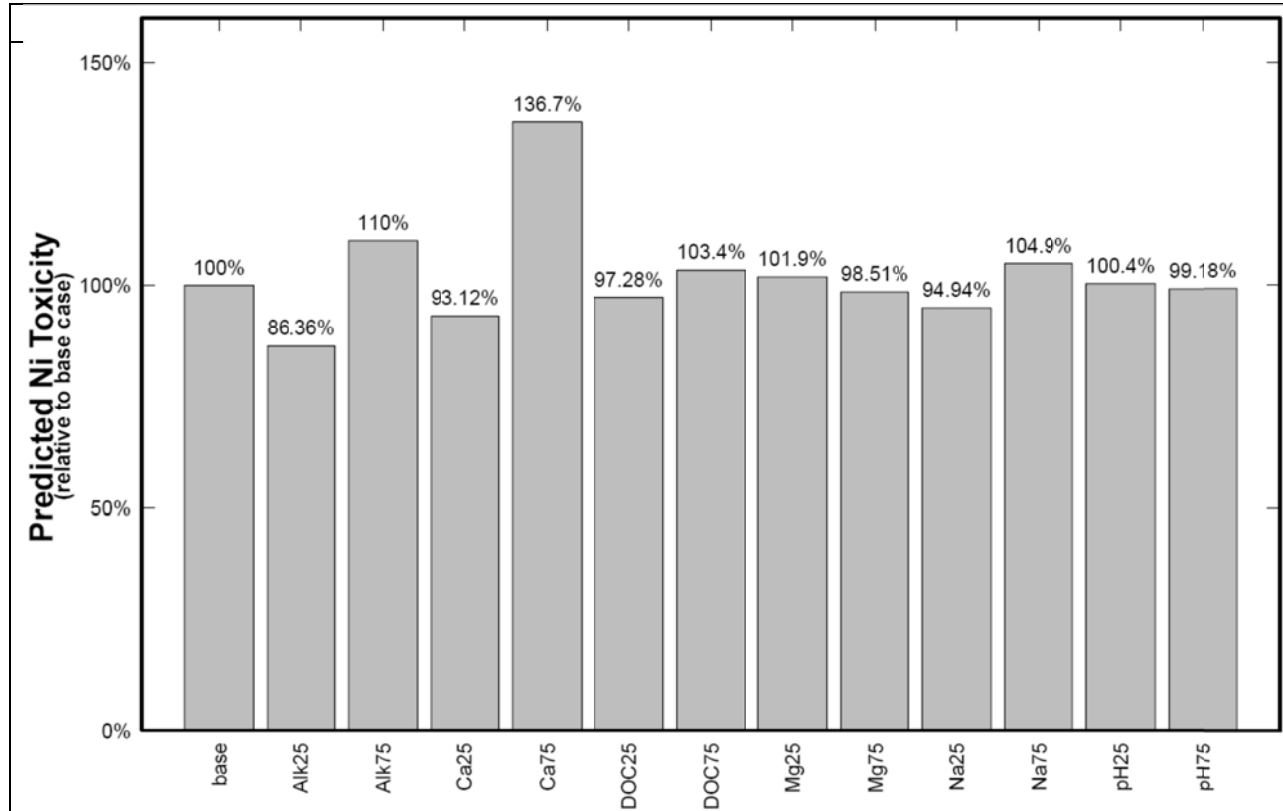


Figure 6. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25<sup>th</sup> or the 75<sup>th</sup> percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25<sup>th</sup> percentile for Alkalinity (shown in Figure 4), and the result “Alk75” uses the 75<sup>th</sup> percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For each BLM parameter, two additional runs were then performed by substituting either the 25% or 75% value from the box and whisker plots in Figure 4 for the average value, while keeping all other parameters constant, at their respective average. The resulting sensitivity analyses are shown in Figure 6 for river samples considering variation at the 25<sup>th</sup> and 75<sup>th</sup> percentile, and Figure 7 considering variation at the 10<sup>th</sup> and 90<sup>th</sup> percentiles.

06/30/2014 - \* \* \* R2014-024 \* \* \*

Variation in input values at the 25<sup>th</sup> and 75<sup>th</sup> percentiles for river water samples had relatively little effect on the predicted Nickel toxicity, with the largest effects resulting from changes in Alkalinity and Calcium concentrations. A similar pattern was observed when variation at the 10<sup>th</sup> and 90<sup>th</sup> percentiles were considered (Figure 7). Even at these extreme values, the expected variation in predicted Nickel toxicity ranges from about 70 to 150 percent of the base case value. Guidance for derivation of site-specific adjustments to WQC based on the WER procedure allow simple geometric means of individual WER values when the range in values is within a factor of 5. Since the effects of the variation in river water chemistry on Nickel toxicity will be well within those limits, this uncertainty analysis supports the conclusion that average conditions from a relatively small number of samples should provide an acceptable characterization for deriving a site-specific Nickel criterion. As a result of these sensitivity analyses, the calculated WER for the site is not expected to significantly change as a result of variability in water quality within ranges comparable to these existing monitoring datasets.

06/30/2014 - \* \* \* R2014-024 \* \* \*

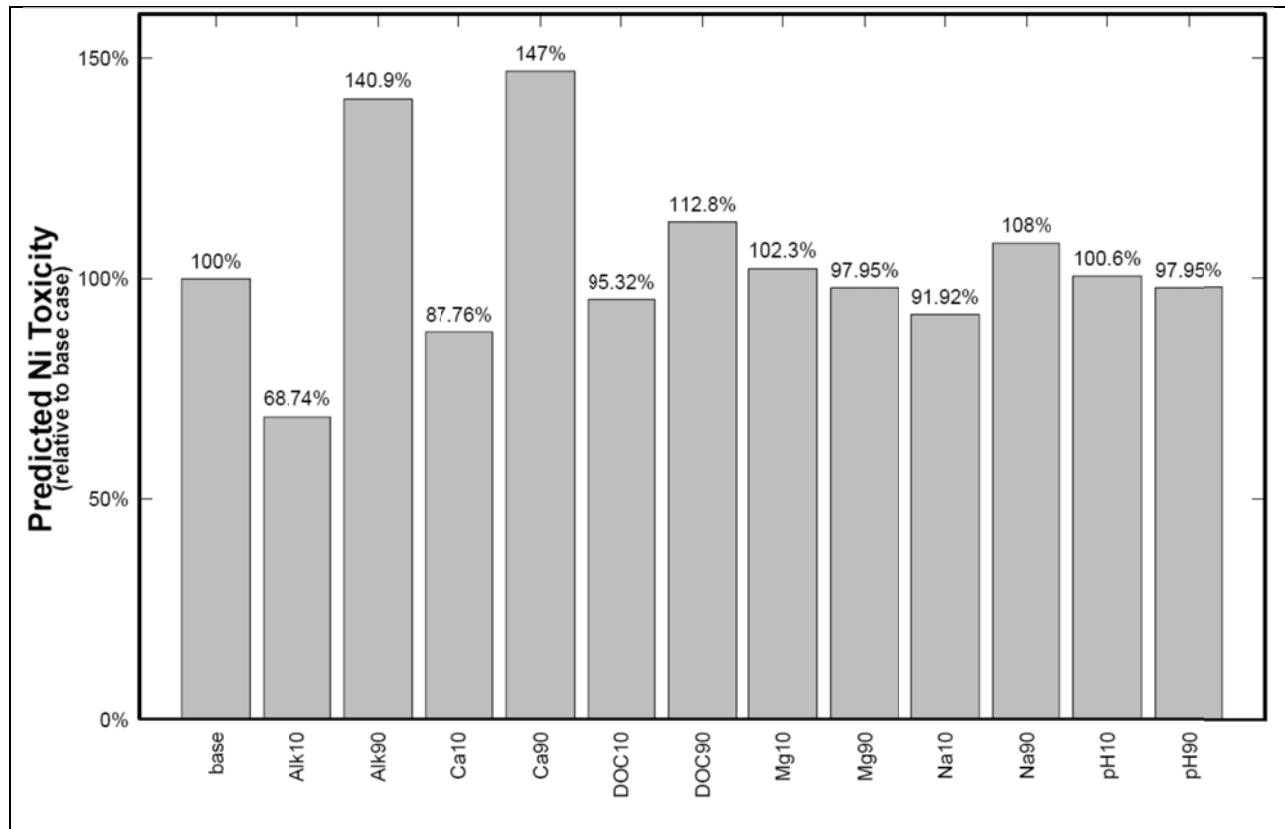


Figure 7. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 10<sup>th</sup> or the 90<sup>th</sup> percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk10” uses the 10<sup>th</sup> percentile for Alkalinity (shown in Figure 4), and the result “Alk90” uses the 90<sup>th</sup> percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For effluent samples (Figure 8), variation in Alkalinity had the largest effect on predicted Nickel toxicity. However, the resulting variation in predicted LC50 values was small, corresponding to a little more than 10% change relative to the base case. Variation in effluent characteristics is only presented for comparison to that seen for river water, since it is only the downstream river water that will be used to estimate the site-specific Nickel adjustment.

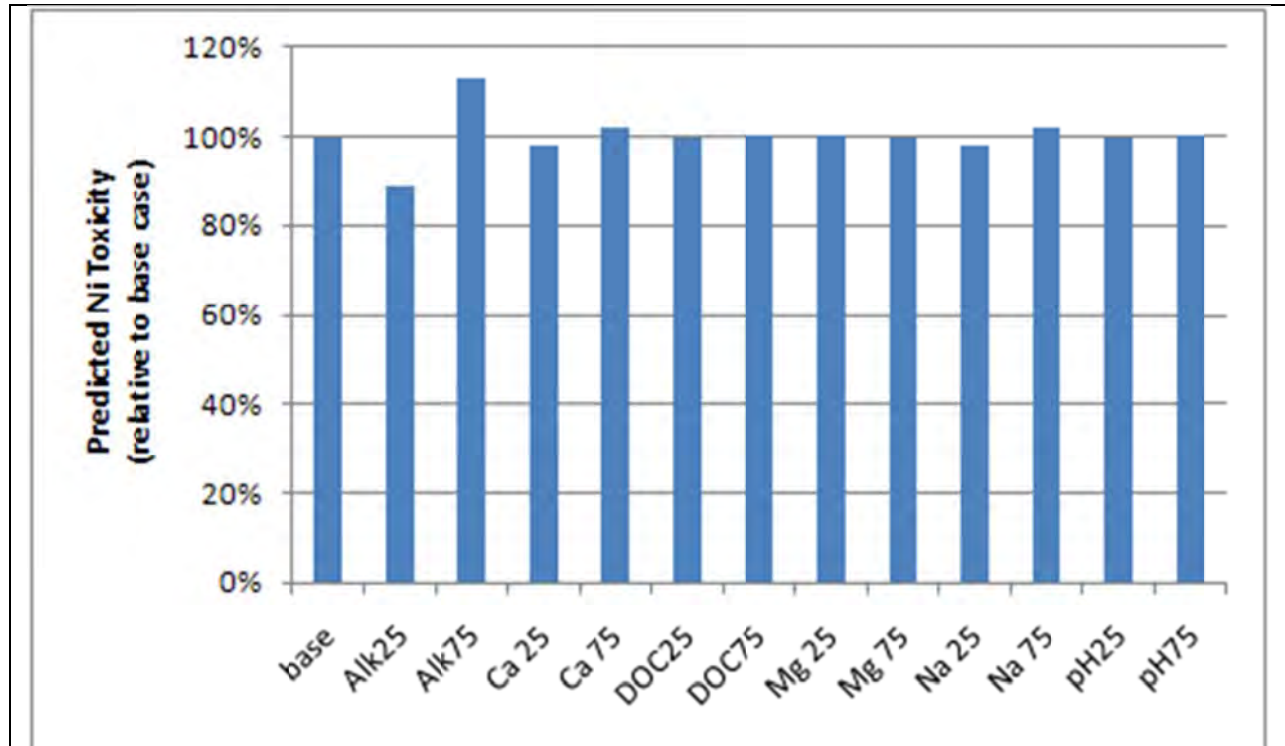


Figure 8. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in effluent samples. For the base case, average values for all parameters shown in Figure 5 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25<sup>th</sup> or the 75<sup>th</sup> percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25<sup>th</sup> percentile for Alkalinity (shown in Figure 5), and the result “Alk75” uses the 75<sup>th</sup> percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.



06/30/2014 - \* \* \* R2014-024 \* \* \*

## VI. PREDICTED ESTIMATE OF WQC

With the WER calculated in Section IV, site specific acute and chronic WQC can be calculated for the site. The site specific criteria are calculated as the state standards times the WER. For the receiving water downstream of the site, the average WER is 2.6, resulting in a site specific acute WQC of 614.1 µg/L and a site specific chronic WQC of 37.2 µg/L (Table 4).

Table 4. Summary of values for corresponding acute<sup>a</sup> and chronic<sup>b</sup> standards, WER, and resulting site specific standards in receiving water samples downstream of the plant. The Illinois acute and chronic standards for Nickel are based on hardness dependent equations. The average for samples collected in this study are based on the average measured hardness in samples collected for the BLM analysis. Also shown are the site-specific values based on a hardness of 359, which was assigned by the State of Illinois for this site.

Sample Date	Sample Location	Hardness	Nickel Acute <sup>a</sup> Standard	Nickel Chronic <sup>b</sup> Standard	Water Effect Ratio	Site Specific Acute Standard	Site Specific Chronic Standard
		mg/L as CaCO <sub>3</sub>	µg/L	µg/L		µg/L	µg/L
8/26	RD at Rock Springs	357	241.7	14.7	2.6	628.5	38.1
9/9	RD at Rock Springs	360	243.5	14.8		633.0	38.4
8/26	RD at Lincoln	332	227.3	13.8	2.6	591.1	35.8
9/9	RD at Lincoln	341	232.5	14.1		604.6	36.6
<b>Average (this study)</b>		<b>347.5</b>	<b>236.2</b>	<b>14.3</b>	<b>2.6</b>	<b>614.1</b>	<b>37.2</b>
<b>Site specific values using Illinois EPA-assigned critical hardness</b>		<b>359</b>	<b>242.9</b>	<b>14.7</b>	<b>2.6</b>	<b>631.5</b>	<b>38.2</b>

Notes:

<sup>a</sup>: Nickel Acute Standard =  $\exp[A+B*\ln(H)] * 0.998$  (where A=0.5173; B=0.846)

<sup>b</sup>: Nickel Chronic Standard =  $\exp[A+B*\ln(H)] * 0.997$  (where A= -2.286; B=0.846)

## **VII. CONCLUSIONS**

Water quality factors such as pH, Alkalinity, ion content, and the presence NOM have been shown to affect metal toxicity. However, the WCQ for many metals consider only hardness, making them potentially over-protective or under-protective for many site waters. The BLM is a mechanistic framework suitable for a number of metals, including Nickel, which allows for the consideration of many additional water quality factors. The BLM has been adopted by US EPA in the most recently updated metals criteria (US EPA, 2007). For metals that do not yet have an approved WQC approach, the BLM can be used to calculate a WER adjustment to derive site specific acute and chronic criteria. Application of the Nickel BLM to calculate Nickel toxicity in samples taken from the Sangamon River downstream of the District's Main Plant compared to a reference water results in a calculated average WER of 2.6. This WER results in a site specific acute criterion of 614.1  $\mu\text{g/L}$  and a site specific chronic criterion of 37.2  $\mu\text{g/L}$  at a hardness equal to 347.5  $\text{mg/L}$ . Utilizing the Illinois EPA-assigned hardness of 359  $\text{mg/L}$ , the WER results in a corresponding acute criterion of 631.5  $\mu\text{g/L}$  and a site specific chronic criterion of 38.2  $\mu\text{g/L}$ .

06/30/2014 - \* \* \* R2014-024 \* \* \*

**VIII. REFERENCES**

Carlson, A.R., W.A. Brungs, G.A. Chapman and D.J. Hansen. 1984. Guidelines for deriving numerical aquatic site specific water quality criteria by modifying national criteria. EPA-600/3-84-099, US EPA, Environmental Research Laboratory, Duluth, Minnesota, USA.

Di Toro, D.M., H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin and R.C. Santore, 2001. A Biotic Ligand Model of the Acute Toxicity of Metals. I. Technical Basis, Environmental Toxicology and Chemistry. 20:2383-2396.

Erickson, R.J., D.A. Benoit, V.R. Mattson, H.P. Nelson, Jr. and E.N. Leonard. 1996. The effects of water chemistry on the toxicity of copper to fathead minnows. Environ. Toxicol. Chem. 15(2):181-193.

Keithly, J; J.A. Booker; D.K DeForest; B.K. Wu, and K.V. Brix. 2004. Acute and Chronic Toxicity of Nickel to a Cladoceran (*Ceriodaphnia dubia*) and an Amphipod (*Hyalella azteca*). Environmental Toxicology and Chemistry. 23(3):691-696

Santore, R.C., D.M. Di Toro and P.R. Paquin, H.E. Allen, and J.S. Meyer. 2001. "A Biotic Ligand Model of the Acute Toxicity of Metals. II. Application to Acute Copper Toxicity in Freshwater Fish and Daphnia," Environmental Toxicology and Chemistry. 20(10):2397-2402.

Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman and W.A. Brungs. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85- 227049. National Technical Information Service, Springfield, VA.

US EPA. 1992. Interim guidance on interpretation and implementation of aquatic life criteria for metals. Health and Ecological Criteria Division, Office of Science and Technology, US EPA, Washington, District of Columbia, USA.

US EPA. 1994a. Water quality standards handbook. 2nd Edition. EPA-823-B94-005b. National Technical Information Service, Springfield, VA.

US EPA. 1994b. Interim Guidance on Determination and Use of Water-Effect Ratios for Metals. EPA-823-B-04-001. National Technical Information Service, Springfield, VA.

US EPA. 2007. Luis A. Cruz, Cindy Roberts, Mary Reiley, Robert Santore, Paul Paquin, Gary Chapman, Jennifer Mitchell, Charles Delos, Joseph Meyer, Rooni Mathew, and Tyler K. Linton. 2007. Aquatic Life Ambient Freshwater Quality Criteria - Copper. 2007 Revision. EPA-822-R-07-001.

WERF. 2003. Development of a Biotic Ligand Model for Nickel: Phase I. KB Wu, PR Paquin, V Navab, R Mathew, RC Santore, DM Di Toro. WERF 01-ECO-10T

06/30/2014 - \*\*\* R2014-024 \*\*\*

## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

December 21, 2011

Illinois Environmental Protection Agency  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

Re: NPDES Permit IL0028321  
IPCB Order PCB 09-125  
Interim Report

Dear Sir or Madam:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 09-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

cc: Rick Pinneo, IEPA (via email)  
Bob Mosher, IEPA (via email)  
SDD File

06/30/2014 - \* \* \* R2014-024 \* \* \*

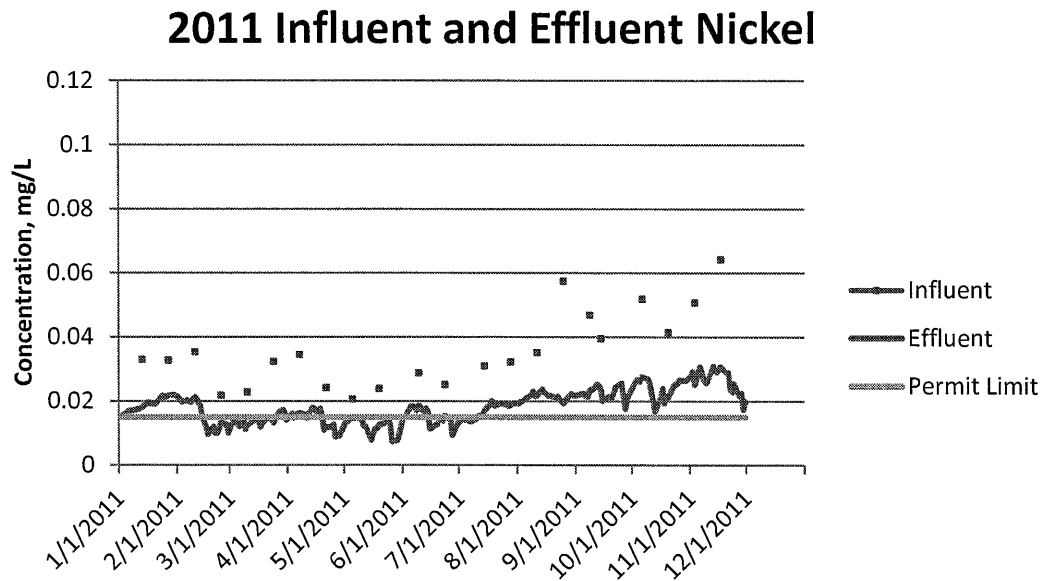
**Sanitary District of Decatur  
Nickel and Zinc Limits  
December 2011 Interim Report**

The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires that an interim progress report be submitted to Illinois EPA by January 1, 2012.

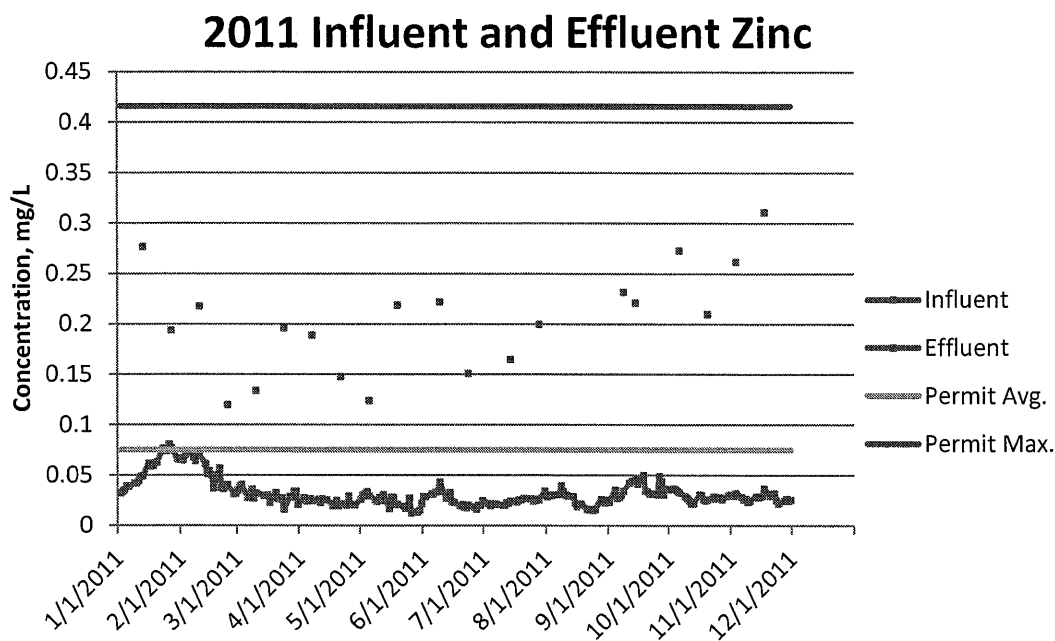
On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified to incorporate the variance although Illinois EPA issued a Public Notice and draft modified permit on May 26, 2011. The Board Order also requires that an interim progress report be submitted by January 1, 2012 and lists a number of other activities and investigations that are to be completed. This report is submitted to meet both the permit and variance requirements.

**Plant Influent and Effluent Sampling**

Ongoing influent sampling for nickel and zinc continues at a frequency of twice monthly, and effluent sampling is done five days per week according to NPDES monitoring requirements. A summary of influent and effluent values during 2011 is shown below. Data shows that the plant effluent is not able to consistently meet the current nickel permit limit. Zinc concentrations remain below the permit limit.



06/30/2014 - \* \* \* R2014-024 \* \* \*



### Receiving Stream Sampling

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. One upstream and four downstream sampling sites are being monitored. A summary of 2010-2011 river monitoring data is attached. Downstream nickel results remain high during times of low upstream river flow. All upstream and downstream zinc results during 2011 have been below the Illinois water quality standard.

### Pretreatment Ordinance Limits

The District's pretreatment ordinance was amended in October 2009 as noted in previous reports.

### Stream Flow-Based Compliance Options

The District continues investigation of flow-based permit limits, to take advantage of upstream flow for mixing when it is available. This concept could potentially allow a savings in treatment facility operating costs when the upstream flow is sufficient to meet water quality standards after mixing with treatment plant effluent. A USGS flow gauging station is located about two miles upstream of the District's discharge point, and provides near- real time flow information. Informal discussions with Illinois EPA personnel have indicated a preference for flow-based limits to be a part of relief requested from the Pollution Control Board.

06/30/2014 - \* \* \* R2014-024 \* \* \*

### **Water Quality Standard Investigations**

The District is continuing to investigate approaches to a water quality standard adjustment including a limit based on a bioavailability approach. SDD staff and personnel from Hydro-Qual have discussed aspects of the proposal with Illinois EPA staff during the past few months. The District is in the final stages of preparing a petition for a site-specific nickel standard, which should be filed with the Pollution Control Board in early 2012.

We are also following the Pollution Control Board rulemaking currently underway to correct an error found in the existing zinc water quality standard.

### **Industrial Source Sampling and Investigations**

Sampling at Archer Daniel Midland Company for metals continues at a frequency of twice monthly and other industries discharging metals are sampled quarterly. Sample results obtained from ADM within the past year are attached.

The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits. Final local limits will be effective upon expiration of the District's variance.

Both ADM and Tate & Lyle formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. District staff met with ADM personnel several times during the second half of 2011, most recently on December 12. The District's pretreatment permit requires semi-annual reports of ADM's investigations, and the most recent report is attached. Work during the past six months has included pilot testing for several nickel removal technologies, toxicity testing to determine potential impacts of the District's nitrification process, and ongoing research into alternative technologies.

### **Additional Pretreatment Limit Investigations**

Pretreatment ordinance limits adopted in 2009 were adopted as total (rather than soluble) limits based on review of soluble/insoluble data. Refinement of pretreatment limits is an ongoing process and will depend on final permit limits as well as treatment technologies that might be employed by industrial users. The required determination of

06/30/2014 - \* \* \* R2014-024 \* \* \*

soluble/insoluble vs. total limits will be updated as part of the final compliance plan submitted to the Agency.

### **Compliance Plan**

In summary, the District's proposed compliance plan includes ongoing work as required by the Board Order granting the District's variance. The District will continue to proceed in accordance with the schedule in the Order with efforts in three areas:

1. Continuing to work with ADM to investigate nickel removal technologies, and to determine a sludge wasting plan that will minimize zinc discharges. The Order lists ten technologies that were to be investigated by December 31, 2010; the investigations were done as required. Additional investigations and pilot studies continue and a summary is attached.
2. Completion and filing a petition for a site-specific water quality standard for nickel, based on bioavailability. Work on the petition is proceeding with a goal of filing early in 2012.
3. Conducting additional discussions with Illinois EPA permit personnel regarding variable permit limits based on the amount of flow available in the Sangamon River. At this time, the District intends to include flow variable limits in its request for a site-specific water quality standard.



Sanitary District of Decatur  
Nickel and Zinc River Data 2010-2011

06/30/2014 \*\*\* R2014-024 \*\*\*

Sample Date	Plant Final Effluent Nickel mg/L	River Up-stream Nickel mg/L	River 100 yds Down-stream Nickel mg/L	River 600 yds Down-stream Nickel mg/L	Steven's Creek Nickel mg/L	River Rock Springs Bridge Nickel mg/L	River Wyckle's Road Nickel mg/L	River Lincoln H'stead Nickel mg/L	Plant Final Effluent Zinc mg/L	River Up-stream Zinc mg/L	River 100 yds Down-stream Zinc mg/L	River 600 yds Down-stream Zinc mg/L	Steven's Creek Zinc mg/L	River Rock Springs Bridge Zinc mg/L	River Wyckle's Road Zinc mg/L	River Lincoln H'stead Nickel mg/L	Plant Final Effluent Flow mgd	River Up-stream Flow ft <sup>3</sup> /sec
1/14/10	0.0202	<0.00131	0.00374	0.00407	<0.00131	0.00331		0.00318	0.0393	<0.00660	0.0102	0.0108	<0.00660	0.00839		0.0112	30.29	208
1/28/10	0.0160	0.00205	0.00253	0.00240	<0.00131	0.00209		0.00237	0.0399	0.0129	0.0130	0.0121	0.00773	0.0135		0.0138	42.87	3470
2/11/10	0.0204	<0.00131	0.00462	0.00357	<0.00131	0.00277		0.00253	0.0344	<0.00660	0.0119	0.00980	0.00789	0.0108		0.00710	31.39	517
2/18/10	0.0304	<0.00131	0.00527	0.00468	<0.00131	0.00398		0.00351	0.0377	0.00696	0.0103	0.0103	0.00790	0.00777		0.00819	33.12	436
3/4/10	0.0235	<0.00131	0.00376	0.00332	<0.00131	0.00242		0.00240	0.0304	0.00667	0.00918	0.00851	<0.00660	0.00746		0.00895	37.82	755
3/18/10	0.0194	0.00133	0.00232	0.00199	<0.00131	0.00165		0.00200	0.0260	0.00781	0.00966	0.00953	0.00739	0.00801		0.0107	39.45	2160
4/15/10	0.0208	<0.00131	0.00290	0.00279	<0.00131	0.00237		0.00281	0.0204	<0.00660	0.00758	0.00867	<0.00660	<0.00660		0.00761	35.89	482
4/29/10	0.0173	<0.00131	0.00186	0.00201	<0.00131	0.00175		0.00222	0.0290	0.00776	0.00676	0.00833	0.0136	<0.00660		0.00902	31.86	728
5/13/10	0.0127	0.00137	0.00195	0.00244	0.00176	0.00174		0.00229	0.0244	0.00762	0.00767	0.00791	0.0121	0.00821		0.0112	38.27	1440
5/27/10	0.0211	<0.00131	0.00388	0.00284	0.00158	0.00226		0.00259	0.0293	0.00765	0.00875	0.00763	0.00872	0.00697		0.00982	37.01	948
6/10/10	0.0229	0.00205	0.00298	0.00241	0.00325	0.00217		0.00291	0.0328	0.0108	0.0106	0.00988	0.0183	0.0105		0.0145	38.57	1820
6/24/10	0.0205	0.00262	0.00620	0.00386	0.00332	0.00311		0.00345	0.0212	0.0144	0.0137	0.0125	0.0174	0.0142		0.0148	72.13	6120
7/8/10	0.0458	<0.00131	0.00637	0.00713	<0.00131	0.00540		0.00571	0.0662	<0.00660	0.0148	0.0175	<0.00660	0.0155		0.0121	34.86	348
7/29/10	0.0433	0.00190	0.00744	0.00600	0.00151	0.00580		0.00600	0.0564	0.00909	0.0132	0.0122	<0.00660	0.0123		0.0248	38.86	285
8/12/10	0.0493	0.00157	0.0367	0.0353	<0.00131	0.0327		0.0338	0.0681	0.0130	0.0578	0.0529	<0.00660	0.0480		0.0601	31.89	24
8/26/10	0.0370	0.0025	0.0319	0.0320	0.00177	0.0294		0.0211	0.0253	0.0130	0.0255	0.0246	<0.00660	0.0221		0.0121	30.59	4.7
9/9/10	0.0269	<0.00131	0.0203	0.0197	0.00135	0.0166		0.0119	0.0314	<0.00660	0.0219	0.0209	0.0113	0.0257		0.0218	32.10	11
9/23/10	0.0192	0.00186	0.0136	0.0132	0.00188	0.00915		0.0108	0.0309	0.0119	0.0590	0.0249	0.0105	0.0188		0.0162	34.19	2.0
10/14/10	0.0182	0.00251	0.0176	0.0182	0.00143	0.0149	0.0152		0.0335	0.00827	0.0335	0.0317	0.00893	0.0259	0.0303		25.66	1.9
10/28/10	0.0238	0.00135	0.0209	0.0212	<0.00131	0.0158	0.0157		0.0261	<0.00660	0.0316	0.0232	<0.00660	0.0179	0.0190		28.28	1.9
11/04/10	0.0227	0.00146	0.0222	0.0223	<0.00131	0.0193	0.0193		0.0474	<0.00660	0.0440	0.0421	<0.00660	0.0367	0.0354		31.01	2.7
11/18/10	0.0207	0.00131	0.0191	0.0189	<0.00131	0.0164	0.0170		0.0287	<0.00660	0.0271	0.0274	<0.00660	0.0245	0.0238		29.94	4.5
12/02/10	0.0203	0.00180	0.00269	0.00217	<0.00131	0.00217	0.00186		0.0396	<0.00660	0.00702	0.00745	<0.00660	0.00779	<0.00660		33.60	1480
12/16/10	0.0199	<0.00131	0.00311	0.00210	<0.00131	0.0017	0.00156		0.0356	<0.00660	0.00672	0.00859	<0.00660	<0.00660	<0.00660		28.51	694
01/13/11	0.0181	<0.00131	0.00519	0.00495	<0.00131	0.00426	0.00504		0.0503	<0.00660	0.0157	0.0152	<0.00660	0.0133	0.0149		29.48	121
01/27/11	0.0218	<0.00131	0.0144	0.0138	<0.00131	0.0113	0.0102		0.0773	<0.00660	0.0504	0.0481	<0.00660	0.0394	0.0350		30.71	3.9
02/10/11	0.0214	<0.00131	0.0141	0.0128	<0.00131	0.0112	0.00971		0.0701	<0.00660	0.0460	0.0413	0.00761	0.0364	0.0313		27.94	5.4
02/24/11	0.0132	0.00160	0.00242	0.00252	0.00150	0.00214	0.00205		0.0406	0.00841	0.0106	0.0108	0.0138	0.0114	0.00992		44.38	1970
3/10/11	0.0123	0.00169	0.00194	0.00198	0.00153	0.00184	0.00208		0.0321	0.00972	0.00978	0.00992	0.0103	0.00974	0.0100		47.51	2900
3/24/11	0.0132	<0.00131	0.00133	0.00133	<0.00131	<0.00131	<0.00131		0.0161	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660		33.28	667
4/7/11	0.0163	<0.00131	0.00343	0.00252	<0.00131	0.00241	0.00237		0.0246	<0.00660	0.00884	0.00689	<0.00660	0.00732	0.00691		30.62	326
4/21/11	0.0118	<0.00131	0.00236	0.00195	0.00254	0.00157	0.00188		0.0215	0.00729	0.00878	0.00822	0.0170	0.00939	0.00934		52.22	2540
5/5/11	0.0147	0.00177	0.00279	0.00238	0.00137	0.00218	0.00223		0.0295	<0.00660	0.00932	0.00862	<0.00660	0.00760	0.00898		41.88	1670
5/19/11	0.0125	<0.00131	0.00211	0.00186	<0.00131	0.00153	0.00150		0.0213	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	0.00777		32.29	1290
6/9/11	0.0187	<0.00131	0.00143	0.00194	0.00183	0.00162	0.00177		0.0434	<0.00660	<0.00660	0.00672	<0.00660	<0.00660	0.0124		29.12	1540
6/23/11	0.0154	0.00210	0.00335	0.00307	0.00154	0.00280	0.00329		0.0203	0.0131	0.0134	0.0138	0.0112	0.0129	0.0155		36.23	800
7/14/11	0.0170	<0.00131	0.0118	0.0116	<0.00131	0.00886	0.00890		0.0242	0.00519	0.0162	0.0171	<0.00660	0.0136	0.0130		27.12	200
7/28/11	0.0188	<0.00131	0.0187	0.0168	<0.00131	0.0158	0.0159		0.0255	<0.00660	0.0279	0.0219	<0.00660	0.0205	0.0207		27.85	2.1
8/11/11	0.0218	0.00143	0.0255	0.0212	<0.00131	0.0204	0.0199		0.0294	<0.00660	0.0576	0.0292	<0.00660	0.0266	0.0271		24.82	1.6
8/25/11	0.0193	<0.00131	0.0187	0.0190	<0.00131	0.0183	0.0189		0.0161	<0.00660	0.0153	0.0158	<0.00660	0.0142	0.0137		24.19	1.1
9/8/11	0.0233	0.00142	0.0208	0.0222	<0.00131	0.0207	0.0196		0.0341	<0.00660	0.0294	0.0303	<0.00660	0.0279	0.0254		27.07	0.15
9/14/11	0.0237	0.00132	0.0231	0.0235	<0.00131	0.0228	0.0231		0.0460	<0.00660	0.0425	0.0438	<0.00660	0.0413	0.0385		28.62	1.9
10/6/11	0.0276	0.00140	0.0263	0.0265	<0.00131	0.0255	0.0259		0.0329	<0.00660	0.0318	0.0314	<0.00660	0.0296	0.0288		23.96	0.75
10/20/11	0.0211	<0.00131	0.0189	0.0195	<0.00131	0.0159	0.0181		0.0260	0.0107	0.0235	0.0238	<0.00660	0.0193	0.0199		23.28	2.8
11/3/11	0.0250	0.00197	0.0277	0.0304	0.00175	0.0260	0.0275		0.0322	0.0115	0.0314	0.0354	<0.00660	0.0281	0.0271		42.99	18
11/17/11	0.0307	<0.00131	0.0281	0.0283	0.00178	0.0273	0.0277		0.0368	<0.00660	0.0285	0.0304	<0.00660	0.0275	0.0247		25.80	1.1
12/1/11	0.0221	<0.00131	0.0177	0.0173	<0.00131	0.0149	0.0149		0.0349	0.00728	0.0245	0.0230	0.00824	0.0207	0.0190		27.64	2.1

Indicates that effluent or river/creek sample concentration exceeds chronic water quality value

06/30/2014 - \* \* \* R2014-024 \* \* \*

SDD Major Industrial Nickel and Zinc Results				
	ADM Point A	ADM Point A	ADM Point D	ADM Point D
Sample	Nickel, Tot	Zinc, Tot	Nickel, Tot	Zinc, Tot
Date	mg/L	mg/L	mg/L	mg/L
6/1/2010	0.0813	0.488	0.12	0.441
6/14/2010	0.0826	0.453	0.104	0.345
7/8/2010	0.148	0.54	0.283	1.07
7/12/2010	0.144	0.528	0.193	0.514
8/2/2010	0.125	0.457	0.172	0.446
8/9/2010	0.126	0.44	0.184	0.474
9/1/2010	0.0766	0.465	0.122	0.469
9/20/2010	0.0744	0.442	0.121	0.649
10/4/2010	0.0781	0.461	0.0938	0.369
10/14/2010	0.162	1.18	0.179	1.18
11/8/2010	0.0524	0.24	0.0646	0.208
11/23/2010	0.13	0.665	0.122	0.413
12/6/2010	0.0715	0.53	0.131	0.581
12/13/2010	0.0649	0.498	0.0774	0.219
1/5/2011	0.0629	0.53	0.0669	0.204
1/10/2011	0.0577	0.495	0.0666	0.188
2/7/2011	0.0836	0.756	0.0892	0.329
2/14/2011	0.0589	0.472	0.0598	0.18
3/7/2011	0.0773	0.447	0.0627	0.128
3/14/2011	0.086	0.51	0.1	0.449
4/4/2011	0.07	0.428	0.0841	0.387
4/20/2011	0.0687	0.33	0.0861	0.347
5/2/2011	0.0712	0.304	0.0809	0.302
5/9/2011	0.06	0.301	0.0712	0.3
6/6/2011	0.0648	0.285	0.0786	0.276
6/13/2011	0.0692	0.293	0.0809	0.314
7/11/2011	0.0542	0.226	0.0625	0.209
8/1/2011	0.0491	0.165	0.0621	0.172
8/8/2011	0.0567	0.215	0.074	0.242
9/1/2011	0.0662	0.285	0.0842	0.327
9/7/2011	0.0684	0.311	0.0884	0.344
10/3/2011	0.094	0.518	0.114	0.515
10/10/2011	0.0643	0.191	0.073	0.189
SDD Ordinance Limit (Avg.)	0.0365	0.45		
SDD Ordinance Limit (Max.)	0.15	1.7		

To: Illinois Environmental Protection Agency                      06/30/2014 - \* \* \* R2014-024 \* \* \*  
Decatur Sanitary District

From: ADM Decatur WWTP

CC: ADM Corn Processing, ADM Oilseeds Processing, ADM JRRRC

Date: December 12, 2011

Re: Status Report Compliance Strategy for 2011 for Decatur Sanitary District and ADM  
Decatur WWTP for waste treatment. (Covers updates post July 6, 2011- date)



06/30/2014 - \* \* \* R2014-024 \* \* \*

**Table of Contents**

Table of Contents .....	2
1 Background.....	3
2 Deliverables .....	10
2.1 Nickel- Proprietary Precipitation Process .....	10
2.2 Nickel- Chemical Precipitation Process Using Carbamates or Organic Sulfides .....	10
2.2.1 Chemtreat .....	10
2.2.2 Hydrite .....	11
2.2.3 Kroff 9011.....	13
2.2.4 Hychem Polymeric DP4.....	14
2.2.5 Nalmet (Nalco) .....	14
2.3 Nickel- Ion Exchange Resin .....	16
2.3.1 Purolite Resin .....	16
2.3.2 Corn Plant Used IX system .....	16
2.4 Nickel and Zinc- Soybean Process Stream Alternative.....	17
2.5 Nickel and Zinc- BioProducts Process Stream Alternative.....	17
2.6 Nickel and Zinc- WWTP Sludge Removal System.....	17
2.7 Nickel and Zinc- Reverse Osmosis.....	17
2.7.1 Technical Feasibility .....	17
2.7.2 Capital and Operating costs. ....	17
2.8 Nickel and Zinc- Sludge (WWTP organism cell wall rupture).....	17
2.9 Nickel and Zinc- Sludge Sales .....	18
3 Review Ceased for Technologies.....	18
4 Polyol waste stream treatment.....	18
5 Appendix A Pilot Plant Trials Update.....	20
6 Appendix B Respirometer and Nitratox Testing.....	25

06/30/2014 - \* \* \* R2014-024 \* \* \*

ADM Research and Decatur Corn Processing have been actively pursuing technologies to remove Nickel (Ni) from its effluent stream released to the SDD treatment plant. Enclosed is a report on the progress ADM has made since the last update issued on July 6, 2011.

## 1 Background

Nickel and Zinc are present in effluent leaving the ADM Decatur Complex Waste Water plant. New effluent limits are proposed which will reduce the discharge limits to 0.0365 ppm for Nickel and 0.35 ppm for Zinc. Of the two metals, nickel is more difficult to remove from the effluent. ADM has conducted 5 plant material balances to understand the sources of Nickel in its internal streams. ADM's Decatur Complex consists of multiple, separate processing plants, which send their wastewater to the on-site wastewater treatment plant ("WWTP") operated by Corn Plant personnel. These processing plants consist of the Corn Wet Mill, BioProducts Plant, Cogeneration Plant, East Soybean Processing Plant, West Soybean Processing Plant, Vitamin E Plant, Corn Germ Processing Plant, Glycols Plant and the Polyols Plant. Each of these unique plants produces multiple products, using both batch and continuous processes, and creates water streams which generally are reused multiple times prior to being discharged to the WWTP. The WWTP treats approximately 11 MGD through a newer anaerobic treatment system followed by aerobic treatment prior to discharge to the District.

The incoming soybeans contain approximately 4.1 parts per million ("ppm") nickel, while incoming corn contains approximately 0.53 ppm nickel. Given that ADM's Decatur Complex processes approximately 600,000 bushels of corn and 200,000 bushels of soybeans per day, our incoming Nickel load is about 49.2 lbs from the Soybeans and 19.1 lbs from the corn. A small portion of the incoming nickel is discharged in the effluent.

The concentration and total quantity coming from the various waste water treatment plant influents from our five plant balances are shown in Table 1 (Total Nickel) and 2 (Soluble Nickel).

<b>Table 1: Average Total Nickel to HIGH SALT in ppm</b>					
	<u>Summer 09</u> balance	<u>Jan-Feb/2010</u> 30 days	<u>Fall 2010</u> 1 day a week for 7 weeks	<u>Jun-Jul/2011</u> 39 days	<u>Fall 2011</u> 5 weeks
Corn Plt		0.104	0.088	0.09	0.13
East Plt		0.195	0.250	0.18	0.24
Bio Prod		0.028	0.028	0.037	0.242
Glycol		0.150	0.106	0.255	0.112
Polyol		0.505	2.5	7.7	9.2
Co-gen		0.011	0.019		
Truck Wash					
<b>Weighted Average</b>		<b>0.121</b>	<b>0.139</b>	<b>0.140</b>	<b>0.154</b>
<b>HS EQ Tank</b>		<b>0.210</b>	<b>0.170</b>	<b>0.137</b>	<b>0.132</b>
<small>(HS EQ Tank is the combined stream of all plants high salt streams)</small>					

06/30/2014 - \* \* \* R2014-024 \* \* \*

<b>Table 2: Average Soluble Nickel to HIGH SALT in ppm</b>					
	<u>Summer 09</u>	<u>Jan-Feb/2010</u>	<u>Fall 2010</u>	<u>Jun-Jul/2011</u>	<u>Fall 2011</u>
	balance	30 days	1 day a week for 7 weeks	39 days	5 weeks
Corn Plt	0.105	0.104	0.092	0.091	0.030
East Plt	0.240	0.161	0.200	0.164	0.180
Bio Prod	0.048	0.028	0.028	0.040	0.030
Glycol		0.150	0.107	0.285	0.110
Polyol		0.476	2.6	8.1	11.1
Co-gen	0.000	0.011	0.017		
Truck Wash					
<b>Weighted Average</b>	<b>0.142</b>	<b>0.107</b>	<b>0.125</b>	<b>0.135</b>	<b>0.110</b>
<b>HS EQ Tank</b>		<b>0.170</b>	<b>0.140</b>	<b>0.090</b>	<b>0.151</b>
<small>(HS EQ Tank is the combined stream of all plants high salt streams)</small>					

The majority of nickel found in ADM effluent water originates in the corn and soybeans being processed at the facility. During the processing, the metals are released and enter the processing water some of which eventually ends up at the wastewater treatment plant.

ADM has monitored soluble Nickel at the Damon and Front stations continuously (see [Figures 3 & 4](#)) and made a number of observations:

- 1) In the past 9 months there has been a decline in Nickel from about 120 ppb to about 60 ppb. However we have experienced severe spikes in effluent nickel in September-November, 2011 each lasting 2-3 days.
- 2) There has been a significant reduction in Soluble Nickel using Diatomaceous Earth (~0.2 $\mu$ ) vs. 5 $\mu$  filtering (see [Figure 1](#)). This suggests the insoluble nickel is very small and may not be removed by metal precipitants.
- 3) ADM sees a large level of carryover from the anaerobic digesters to the aerobic Dissolve Air Floatation units (DAF). (Figure 2)

As discussed below, ADM is investigating other opportunities for processing the Soy Molasses stream from the East Plant. This will reduce the nickel load from the WWTP.

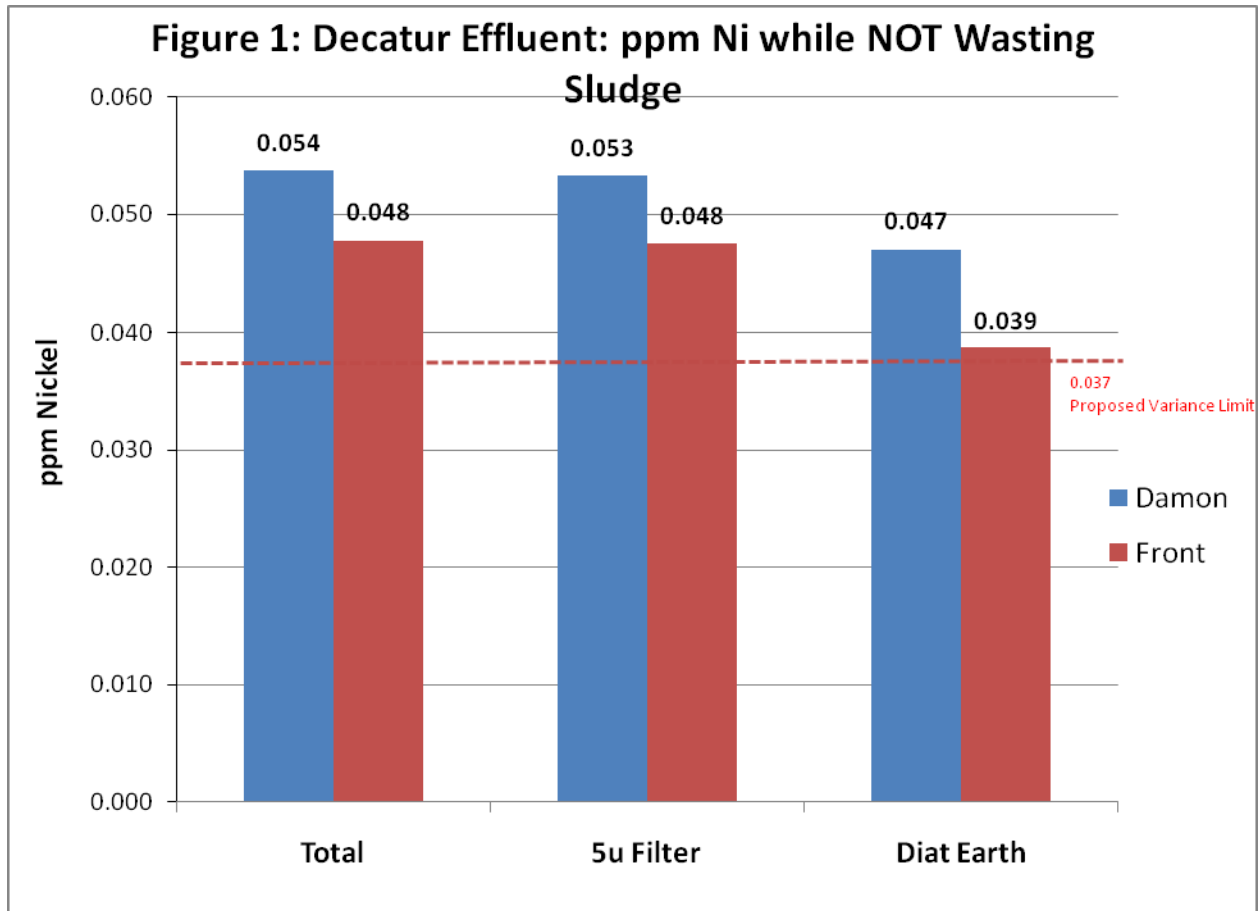


Figure 1: Reduction in DAF Nickel using 0.25 micron DE

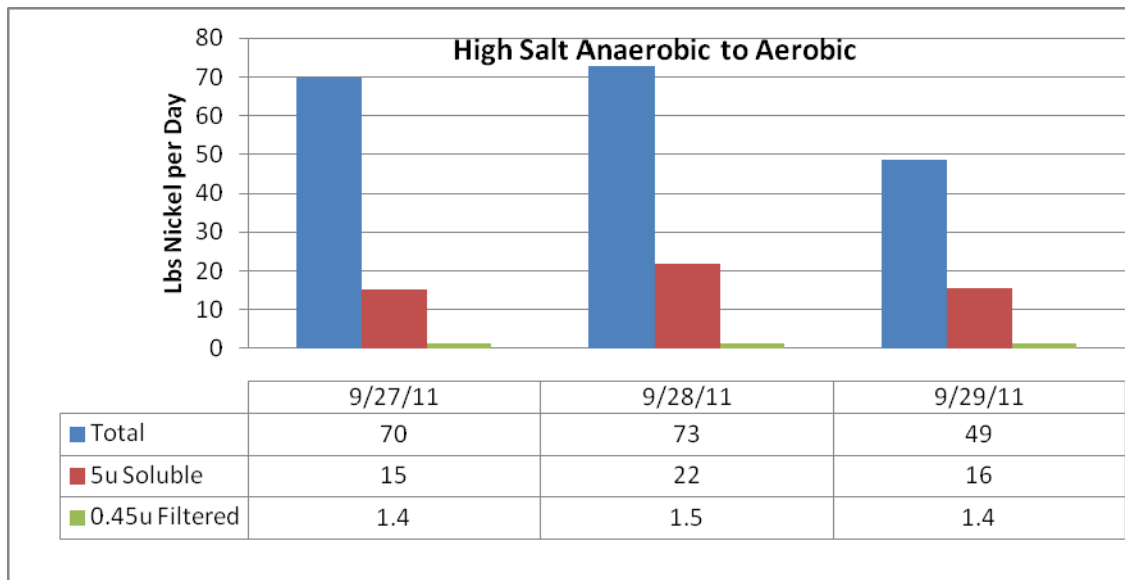


Figure 2: Nickel carryover from Anaerobic digesters

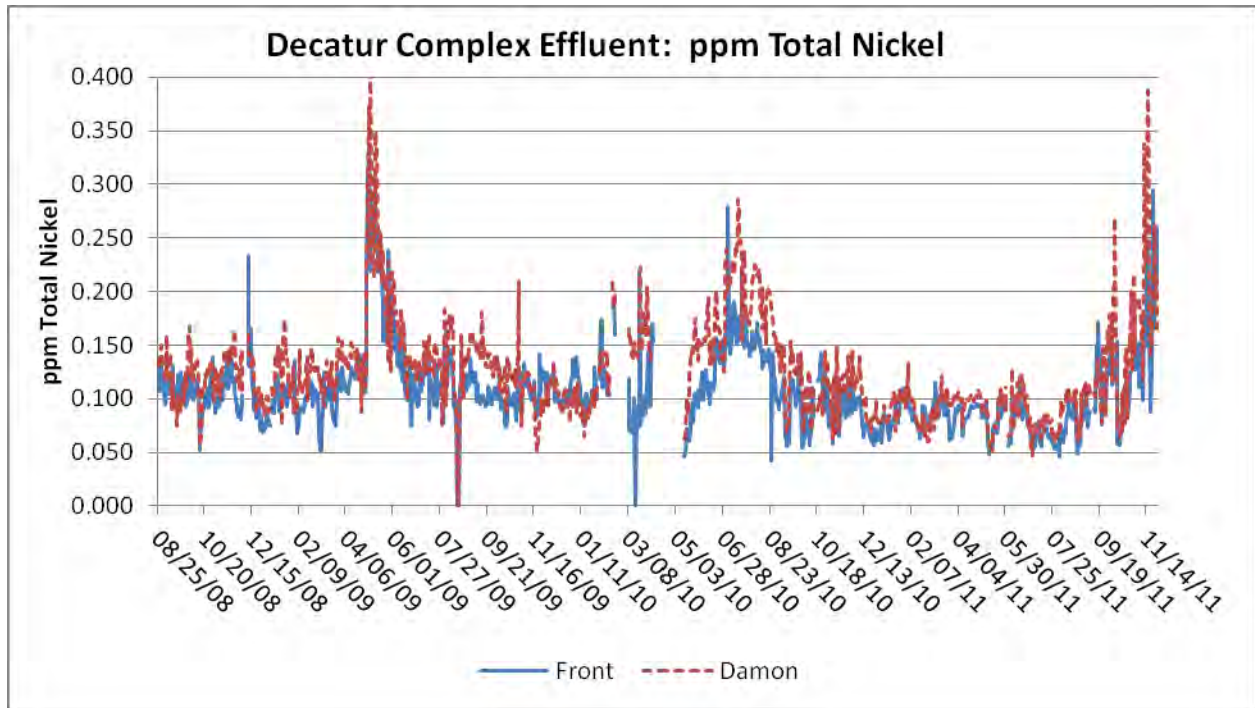


Figure 3: Decatur Complex Effluent- Total Nickel

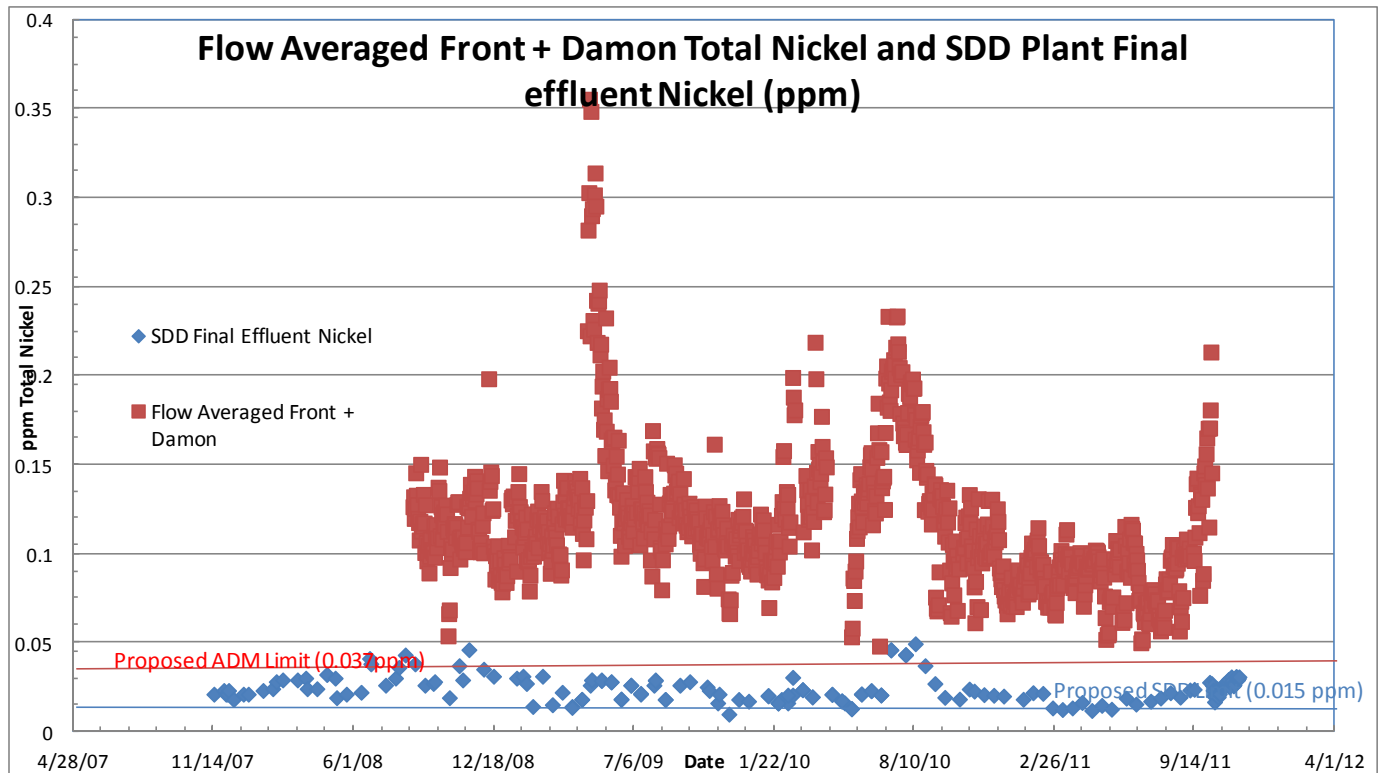


Figure 4: Decatur Complex Effluent- Flow-weighted total Nickel vs. SDD plant effluent total nickel.



06/30/2014 - \* \* \* R2014-024 \* \* \*

As reported in the 2010 and July 2011 updates, ADM has, thus far, investigated 29 technologies that had the potential to control nickel at the Decatur Complex WWTP. (This was in addition to the work ADM has undertaken to reduce nickel within the individual wastewater streams.) As indicated in Table 3, these technologies can be segregated into six broad categories:

1. Nickel Proprietary Precipitation Process;
2. Nickel Chemical Precipitation;
3. Ion Exchange Resin;
4. Filtration;
5. pH Modification
6. Noncommercial, Experimental Technologies.

<b>Table 3: Summary of Technologies Reviewed by ADM Research (12/1/11)</b>					
	Chemistry	Dosage	Nickel Reduction (%)	Current Status	Nitratox / Respirometer Testing*
<b>Nickel Proprietary Precipitation Process</b>					
1. Ecovu	Activated Clay	1%-3% w/w	40-60% (from 200ppb)	Shelved. Unable to scale up	Not tested
2. EP minerals	Acidic Clay	4-8% w/w	40 % (from 90ppb)	Shelved. High dosage	Not tested
3. Crystal Clear Technologies	Chitosan Based	5% w/w	90%	Shelved. High dosage	Not tested
4. Siemens / Plymouth Technologies	Proprietary	2% w/w/	82% (from 100ppb)	Shelved. Company went out of business	Not tested
5. GE Water	Metclear	200 ppm	64%	Shelved. Strong pH swing (acidification to pH 2, alkalination to 10 and neutralization)	Not tested
6. KML	Not disclosed	Not disclosed	58%	Shelved. Company not sharing samples.	Not tested
<b>Nickel Chemical Precipitation</b>					
1. Chemtreat	Polymeric Di methyl Dithiocarbamate	100 ppm + 50 ppm CaCl <sub>2</sub>	30%	Piloted. Nickel reduction seen to 60ppb.	Passed
2. Hydrite	Polymeric Di methyl Dithiocarbamate	20-50ppm	60%	Piloted. Nickel reduction seen to 54 ppb	Passed
3. Kroff	Polymeric Di methyl Dithiocarbamate	100ppm	41%	Piloted. Nickel reduction seen to 32 ppb	Passed
4. Hychem DP4	Di methyl Dithiocarbamate	50ppm + pH 6.0	24%	Piloted. Nickel reduction seen to 40ppb	Passed
5. Nalmet	Polymeric Di methyl Dithiocarbamate	300ppm + pH swing	30%	Shelved. Strong pH swing needed	Not tested
6. Nalmet (Modified)	Polymeric Di methyl Dithiocarbamate	100ppm	48%	Piloted. Nickel reduction seen to 20ppb	Passed
7. Hychem Poly DP	Polymeric Di methyl Dithiocarbamate	200ppm	52%	Piloted. Nickel reduction seen to 39 ppb	Failed.

06/30/2014 - \* \* \* R2014-024 \* \* \*

8. GE Betz DTC	Polymeric Di methyl Dithiocarbamate	100 ppm	40-60%	Not piloted. GE does not have commercial quantities available	Not tested
9. Nalco DTC	Di methyl Dithiocarbamate	100ppm	60%	Piloted. Nickel reduction seen to 24ppb	Passed
<b>Ion Exchange Resin</b>					
1. Purolite	Styrene Di vinyl benzene	2% w/w	20%	Not scaled. High regeneration costs	Not tested
2. Dow	Styrene Di vinyl benzene	4% w/w	60%	Not scaled. Very high resin use. Caustic/ ethanol based regeneration.	Not tested
3. Vivenano	Immobilized Ion Exchange beads	5%	Not significant	Shelved.	Not tested
<b>Filtration</b>					
1. Nalco-RO	Phosphate ppt+ Reverse Osmosis	80% recovery	95+% reduction	Shelved. Uncertainty about treating RO concentrate stream. Capex [REDACTED]	Not tested
2. Filtration Energy Solutions	Low pressure Reverse Osmosis	30% recovery	95% reduction	Shelved. Uncertainty about treating RO concentrate stream. Capex [REDACTED]	Not tested
3. Sand filtration (Procorp)	Sand filter	Not disclosed	20% reduction	Shelved. Insufficient efficacy	Not tested
<b>Other Approaches</b>					
Captive Deionization	Carbon Aerogels	Not tested	Not tested	Company went out of business. Also technology picks up all ions	Not tested
Electrocoagulation	Electrochemical	Not disclosed	Higher Ni seen	Shelved.	Not tested
Salt Precipitation	Ferric Chloride	100ppm	40%	Unscalable due to higher chloride in our wastewater	Not tested
Bioactive Peptides	Protein based	---	Not significant	Lab scale technique only.	Not tested
Advanced Oxidation	Hydrogen Peroxide and Ozone	5% w/w + pH adjustment	20%	High pH required. Chemical usage significant	Not tested
Metallothionein	Protein based	Bench scale	Not tested	Nickel competes for binding with other divalent	Not tested
Acidification/ Alkalinization based precipitation	pH Swing	Bench Scale	30%	pH swing to 10 followed by to 2.0 and back to 7 is required. Very high chemical usage	Not tested
High pH precipitation	pH >11.0	Bench Scale	100% for Polyol waste	High pH precipitation for inorganic nickel from polyol waste stream.	Not required

\*ADM has been working with Riverbend Laboratories in St. Charles, Missouri, to perform respirometer and nitratox testing on various chemistries using MLSS from the District. Such testing is necessary to determine whether the treated effluent is compatible with the District's treatment processes.

ADM continues to operate its pilot plant for chemical sequestration of nickel as needed. We are also planning to start a new pilot reactor at the High Salt equalization tank (HS EQ Tank) to test polymeric treatment of nickel ahead of the anaerobic digesters. [Figures 5&6](#) are pictures of the pilot plant. There are 4 separate mixing tanks of 100 gallons each, using the Decatur plant DAF effluent as feed, with the respective chemistries at various dosages (10-200ppm) and a combination of residence times (1-4 hrs). HS EQ Tank is running a single 100 gallon reactor with one chemistry. One of the setups

06/30/2014 - \* \* \* R2014-024 \* \* \*

was modified to allow for a change in pH and testing of the chemistry at a different pH is scheduled for December 2011. The results from the pilot plant were previously reported on. Since Fall 2011, the chemicals being investigated at the pilot plant have been narrowed to those from Nalco and Hydrite.



Figure 5: ADM Decatur Nickel Removal pilot plant (5/13/2011). Four 100 gal reactors.



Figure 6: High Salt EQ Tank pilot plant. One 100 gallon reactor.

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Pilot testing protocol:**

- 4 mixing tanks; initially 100 gallons liquid level in each in pilot plant
- 1 mixing tank; 100 gallons liquid level
- Two different products to be tested in each tank (currently, Nalmet, Hydrite) at the pilot plant. One chemistry at the HS EQ Tank.
- Feed flows, chemical dosages and agitation can be optimized independently in each tank.
- Ability to adjust residence time in each tank to 0.5 to 8 hrs, through the adjustment of feed flow and tank liquid level
- Ni Precipitant is added in-line in the influent flow and further mixed/reacted in tank.
- Precipitant dosages planned: 10-200 ppm
- Piloting will continue as needed.
- Treated samples from each tank will be filtered through diatomaceous earth (DE) in the lab and submitted to ADM's lab for ICP analysis.
- We expect to use flocculants and coagulants after treatment with metal precipitant.
- pH is monitored in the feed tank but will not be adjusted initially. One tank has been modified for pH adjustment.
- The toxicity studies (by Riverbend Laboratories) on treated wastewater provided the desired Ni removal at current and peak Influent Ni levels.
- Secondary treatment such as DE/Clarifier/Sand filter will be implemented next month.

As required by the variance, a summary of the various control strategies is presented in Appendix B.

*"By July 1, 2011 the District must complete the following tasks:*

*i. Compile various control strategies based on one or more of the feasible technologies. Develop flow diagrams depicting removal options, pros and cons, capital expenditures, and operating costs.*

*ii. Present findings to ADM division managers"*

**- ADM / SDD Variance, p. 41.**

ADM met with the SDD and IEPA on July 8, 2011 and provided them with a copy of the report detailing the progress and ADM's compliance efforts.

## **2 Deliverables**

### **2.1 Nickel- Proprietary Precipitation Process**

As reported previously ADM is no longer pursuing the eight technologies we investigated in this area.

### **2.2 Nickel- Chemical Precipitation Process Using Carbamates or Organic Sulfides**

#### **2.2.1 Chemtreat**

A 33% reduction resulted with P8007L from Chemtreat. No any additional work beyond what was reported in July 2011.

06/30/2014 - \* \* \* R2014-024 \* \* \*

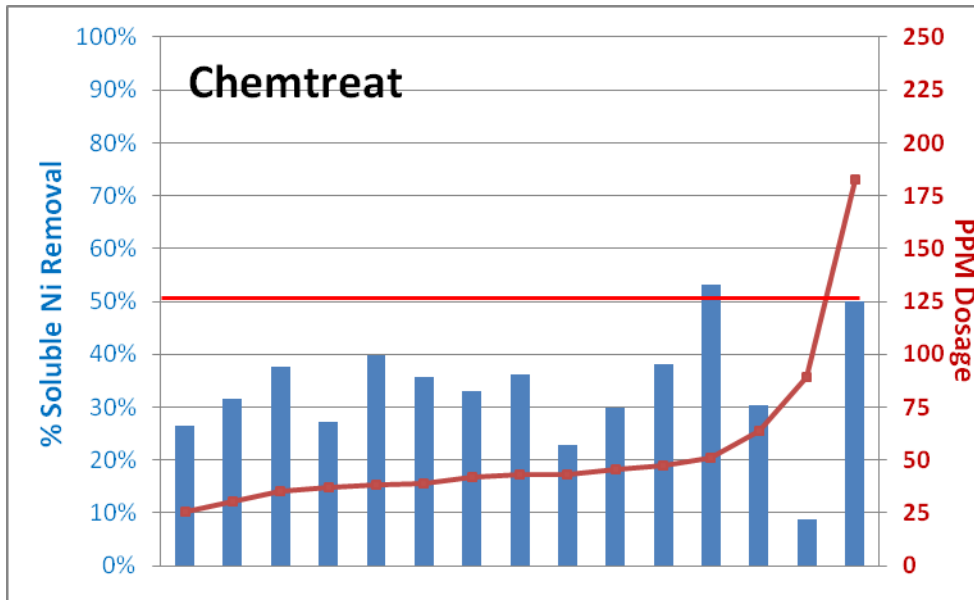


Figure 7: Nickel reduction using Chemtreat P8007L

#### 2.2.1.1 Technical Feasibility

Commercially available product. No problems are expected.

#### 2.2.1.2 Capital and Operation Costs

Chemtreat estimates costs for P8007L at about █████\$/lb.

#### 2.2.1.3 Reliability

ADM has reproduced some of Chemtreat's work internally and plan to conduct a pilot trial with their material. **To date, Chemtreat P8007L has not been piloted.**

#### 2.2.2 Hydrite

Hydrite 1740 is currently being tested in the Pilot plant. A 41% average reduction in soluble nickel has been seen using the 1740 as seen in [Figures 8 and 9](#).

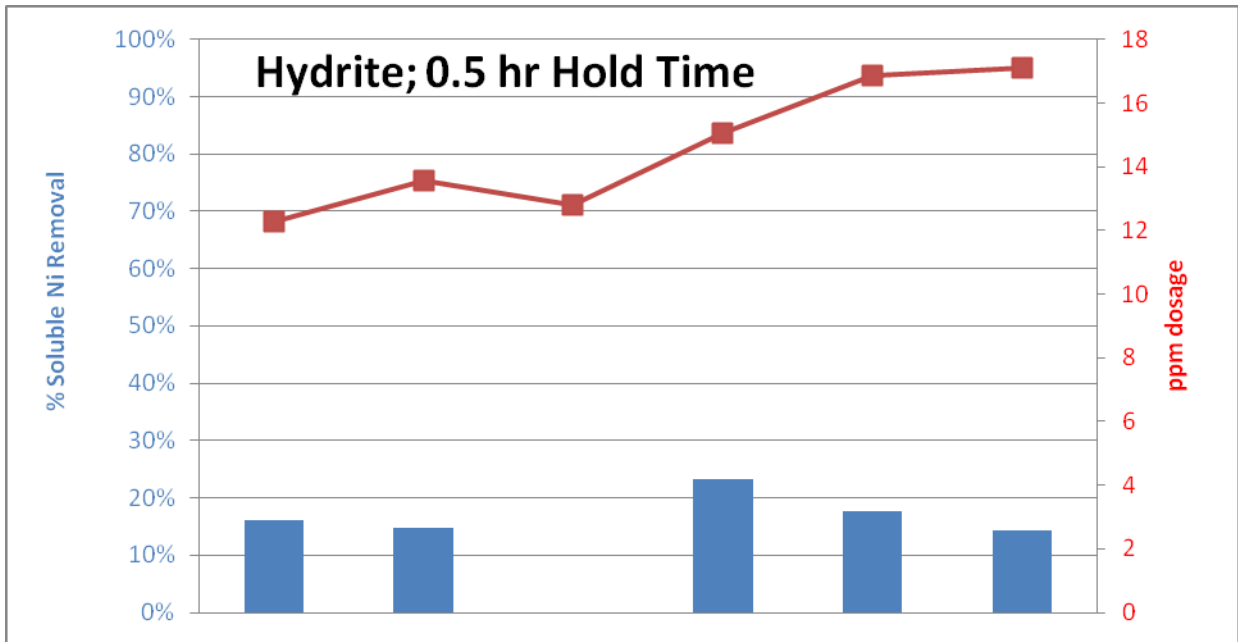


Figure 8: Nickel reduction with 0.5 hr hold time at DAF Pilot plant using Poly DTC from Hydrite.

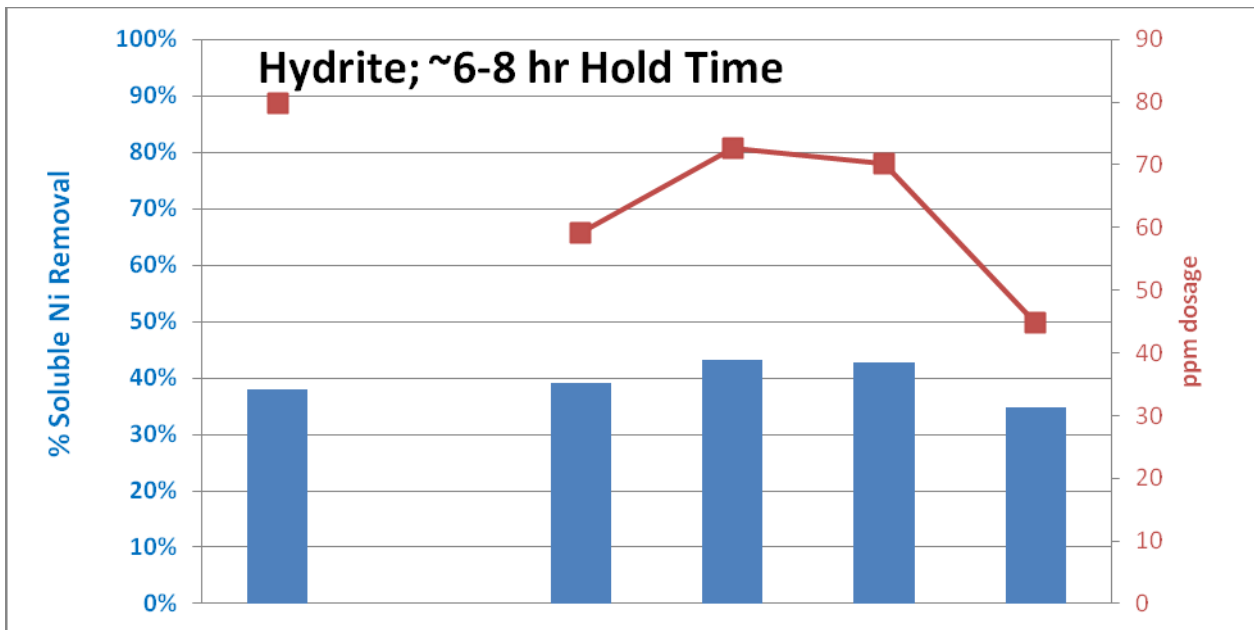


Figure 9: Nickel reduction with 8 hr hold time at DAF Pilot plant using Poly DTC from Hydrite.

**2.2.2.1 Technical Feasibility**

The product is approved for use in waste water systems. Nitratox and Respirometer testing were performed on the waste water at two different dosages of Hydrite (20ppm and 200ppm) and no adverse effects were seen at either dosage.

**2.2.2.2 Capital and Operation Costs**

Hydrite estimates costs at about \$ [redacted] per lb.

**2.2.2.3 Reliability**

Good reproducibility was seen with different feed samples.

**2.2.3 Kroff 9011**

Kroff 9011 is being trialed at the Pilot plant. About a 41% average reduction in soluble nickel was seen using the Kroff 9011 as seen in [Figure 10](#) and [11](#).

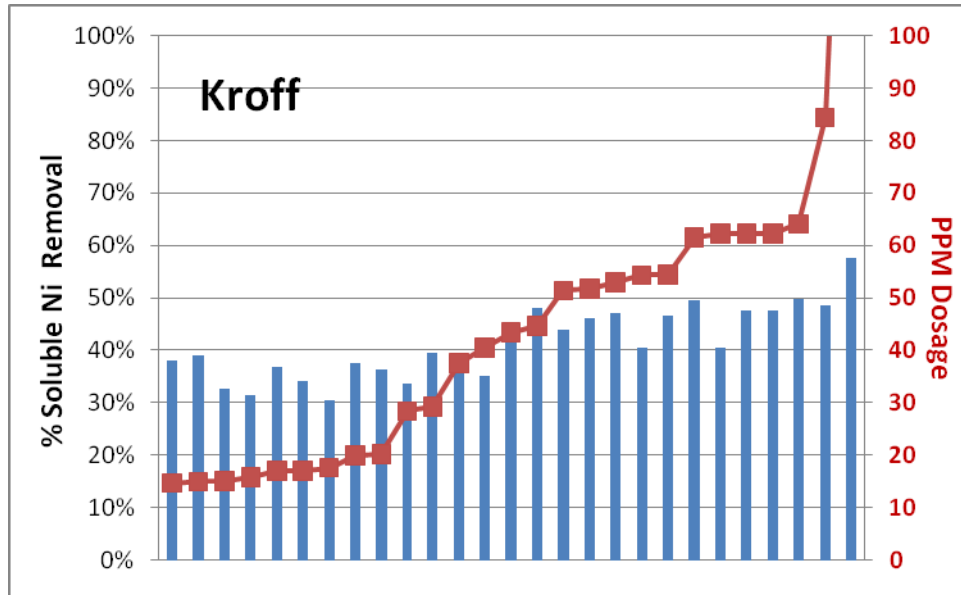


Figure 10: Nickel removal (left scale) and ppm soluble nickel (right scale) with Kroff 9011

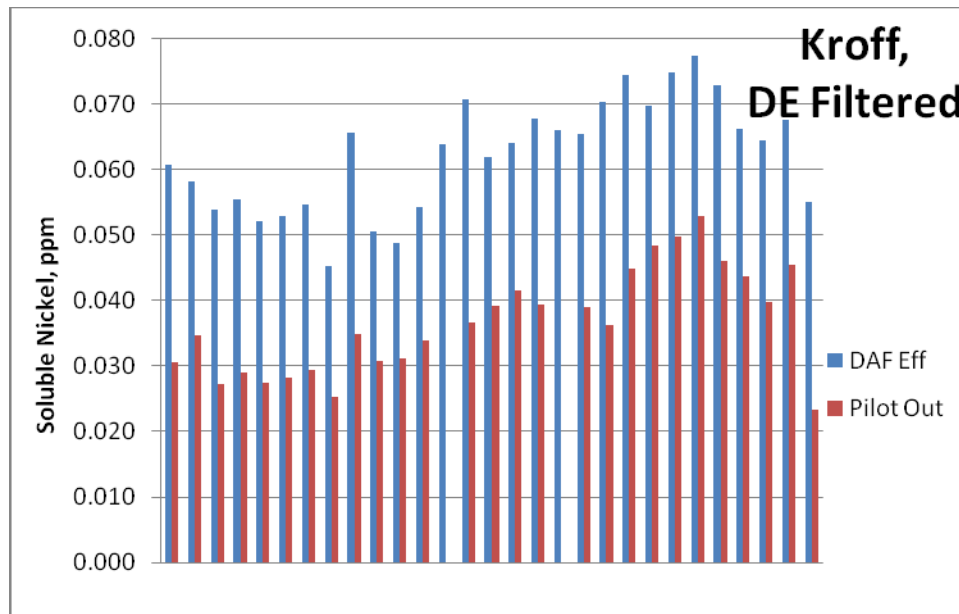


Figure 11: Effect of DE filtration on reduction in soluble nickel after application of 9011

### **2.2.3.1 Technical Feasibility**

No pH adjustment is required. Product is approved for use in waste water systems.

### **2.2.3.2 Capital and Operation Costs**

Kroff estimates costs at about \$█ per lb.

### **2.2.3.3 Reliability**

There has been good reproducibility with different feed samples. Nitratox and Respirometer testing were performed on the waste water samples at two different dosages (20ppm and 200ppm) and no adverse effects were seen at either dosage.

## **2.2.4 Hychem Polymeric DP4**

Hychem Poly DP4 is a polymeric dimethyl dithiocarbamate and was one the first chemistries found that resulted in a nickel reduction. Hychem DP4 is currently being run in the pilot plant. Since the tests are running at "as-is" pH (~8.0) and about a 38% reduction in soluble nickel is being achieved.

### **2.2.4.1 Technical Feasibility**

ADM is not further investigating Hychem poly DP4 at present, as the levels of nickel reduction seen were not significant. Also when we performend respirometer and nitratox studies on the Hychem Poly DP4 treated waste water samples using the SDD MLSS , the samples exhibited nitratox toxicity and less reduction in soluble ammonia levels.

### **2.2.4.2 Capital and Operation Costs**

Hychem poly DP4 is estimated to cost about \$█ per lb.

### **2.2.4.3 Reliability**

There has been good reproducibility with different feed samples, and ADM has tested this chemical in-house the longest. In addition to the "as-is" testing, this chemistry will be tested at pH 6.0 in the pilot trials. Nitratox and Respirometer testing were performed on the treated waste water at two different dosages of DP4 (20ppm and 200ppm) and no adverse effects were seen at either dosage.

## **2.2.5 Nalmet (Nalco)**

As reported in December 23, 2010, work has been done with a new chemistry from NALCO. This chemistry has been piloted at the pilot plant and has resulted in a 48% reduction in soluble Nickel as found in [Figures 12 and 13](#). We also tested Alum and Ferric based coagulants from Hychem following addition of the Nalmet polymer to the waste water and binding of nickel to remove the flocs with a 0.2um filter. We found that Alum based flocculants performed better than Ferric based flocculants (Table 4). This approach will be scaled up when we run pilot equipment using the Nalmet chemistry.



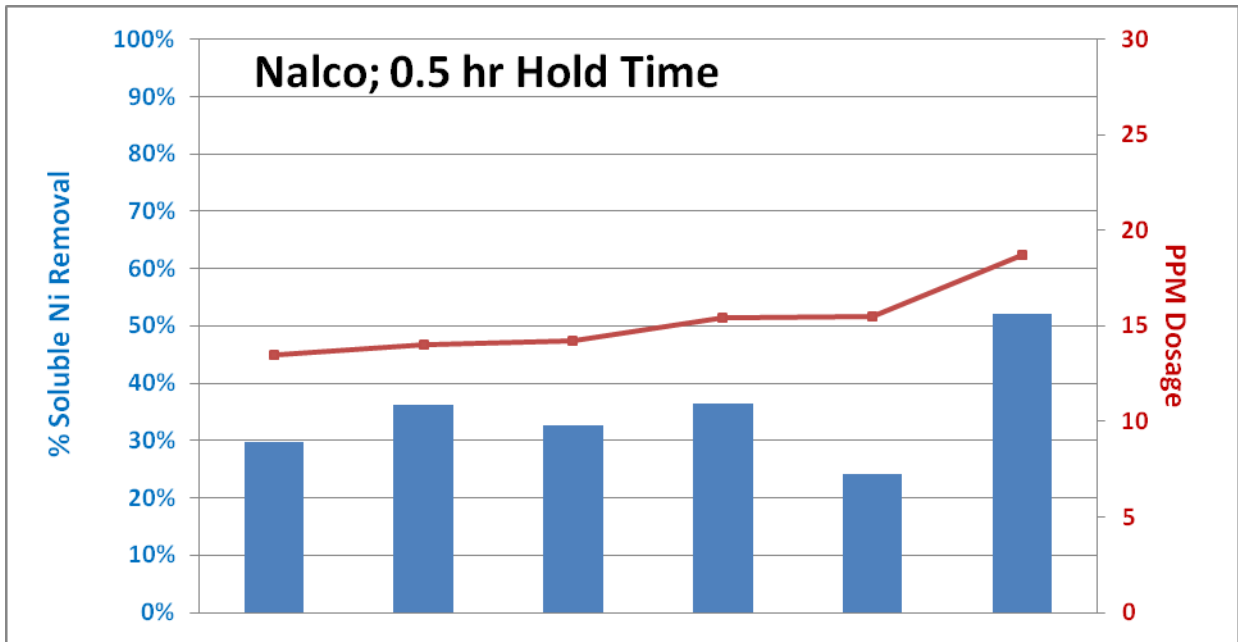


Figure 12: Nickel reduction with 0.5 hr hold time at DAF Pilot plant using Poly DTC from Nalco.

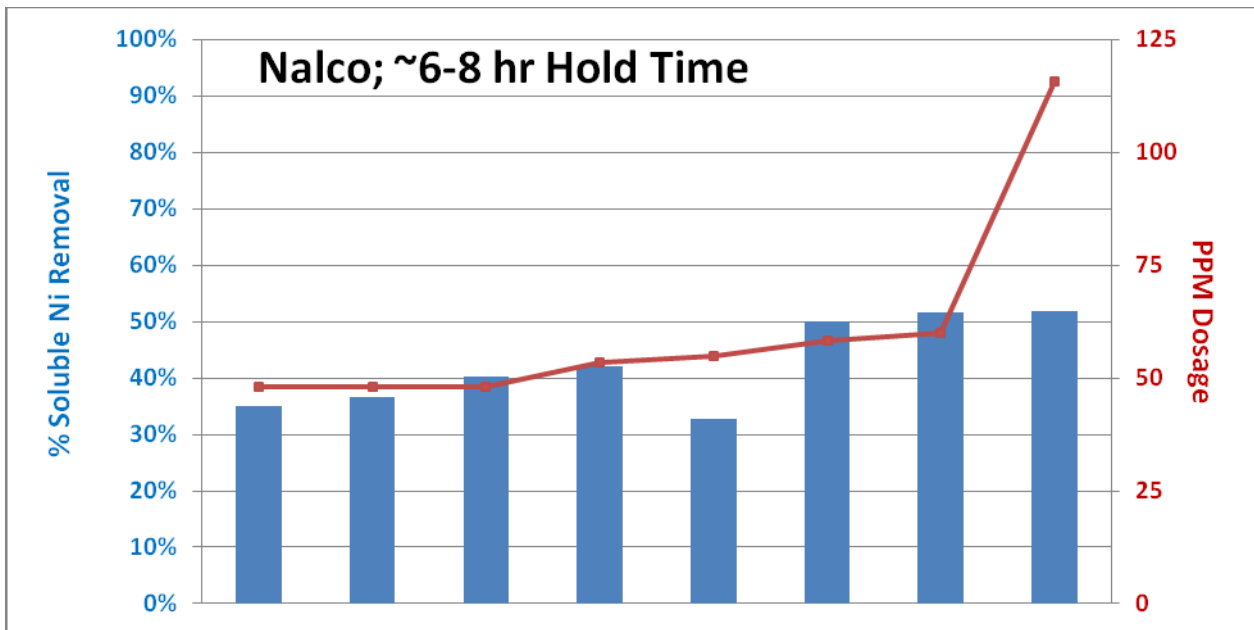


Figure 13: Nickel reduction with 0.5 hr hold time at DAF Pilot plant using Poly DTC from Nalco.

Table 4. Ni removal with Nalmet followed by Hychem 420 Coagulant & 308 Flocculent

	Total Ni (mg/kg)	Soluble Ni (mg/kg)	Total Ni Reduction (%)
DAF Effluent Feed	0.083	0.071	---
Effluent 0.2 micron	0.051	0.051	38.6
HN-18 Test	0.062	0.054	25.3

### 2.2.5.1 Technical Feasibility

Nalmet is not a commercial product, and Nalco's plans to manufacture it commercially are uncertain. No pH adjustment is needed and a very short mixing time is possible. The chemistry does produce a very small size floc, and it is expected to be challenging to remove the floc subsequent to nickel binding.

### 2.2.5.2 Capital and Operation Costs

Costs are estimated at \$█ per lb (N1689/N7768).

### 2.2.5.3 Reliability

There has been good reproducibility with different feed samples. Nitratox and Respirometer testing were performed on the treated waste water samples at two different dosages of Nalmet (20ppm and 200ppm) and no adverse affects were seen at either dosages.

## 2.3 Nickel- Ion Exchange Resin

### 2.3.1 Purolite Resin

As reported in the July 2011, ADM is discontinuing further investigation of a brand new resin system for the entire complex. The efforts on ion exchange will focus on small used resin systems located at strategic inorganic nickel sites (such as the Corn Plant or the Polyols plant).

### 2.3.2 Corn Plant Used IX system

As previously disclosed, ADM has been working to install a used ion exchange resin bed system to capture nickel leaching from the sorbitol process catalyst. This system has been running manually for the past 6 weeks. Thus far, about 5 lbs of nickel have been removed from the treated stream and no nickel has been detected in the effluent. This is shown in [Figure 14](#). We are using 105 cu ft of resin and expect a nickel binding capacity of about 3.4 lbs per cubic ft.

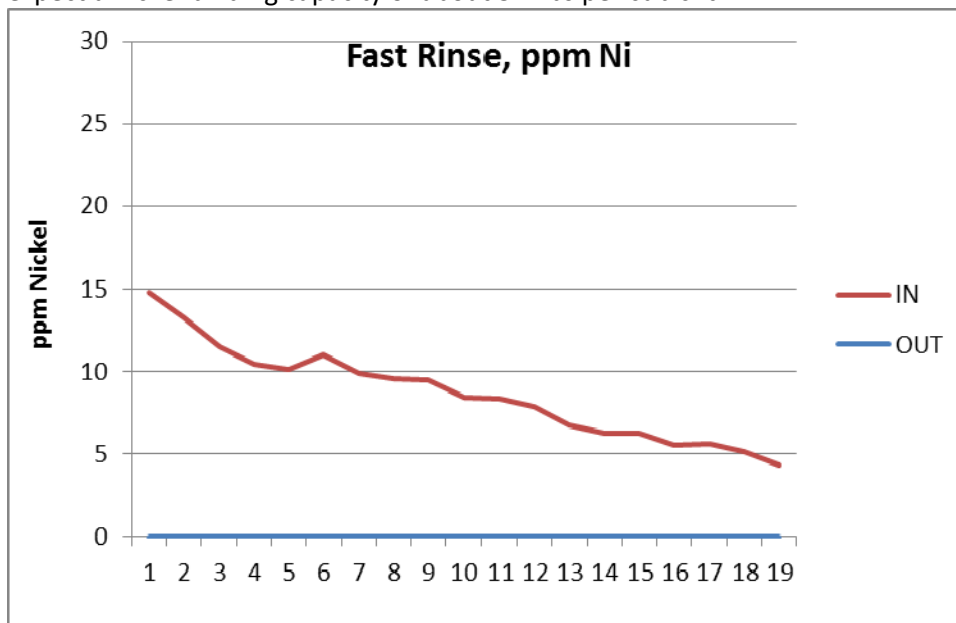


Figure 14: Used ion exchange resin treating material leaving the sorbitol process

06/30/2014 - \* \* \* R2014-024 \* \* \*

### **2.3.2.1 Technical Feasibility**

A full scale system has been installed to capture bulk of the leaching nickel from the sorbitol catalyst.

### **2.3.2.2 Capital and Operating costs.**

About \$ [REDACTED] was spent to install the system and ongoing maintenance and operation costs are expected.

## **2.4 Nickel and Zinc- Soybean Process Stream Alternative.**

Alternatives will be continued to be evaluated for this stream. There has been interest in several companies for purchasing this particular stream for a de-nitrification application in municipal waste treatment plants in the Eastern United States.

## **2.5 Nickel and Zinc- BioProducts Process Stream Alternative**

There have no updates from the report of December 23, 2010.

## **2.6 Nickel and Zinc- WWTP Sludge Removal System**

This process has been investigated and there are no updates from the report of December 23, 2010.

## **2.7 Nickel and Zinc- Reverse Osmosis**

There have been no updates from the report of July 8, 2011.

### **2.7.1 Technical Feasibility**

We have seen very poor recovery and do not expect this process to be scaled up.

### **2.7.2 Capital and Operating costs.**

The estimated capital for a UF/RO/Thermal evaporation based on a ADM's 6 million gallon per day stream is [REDACTED]. However, this capital expense was estimated based on 85% recovery in UF and 75% recovery in RO. As discussed here, the best cases of UF recovery achieved are 60-70% and RO only about 30% due to scaling.

## **2.8 Nickel and Zinc- Sludge (WWTP organism cell wall rupture)**

There are no updates from the report of December 23, 2010.

06/30/2014 - \* \* \* R2014-024 \* \* \*

## 2.9 Nickel and Zinc- Sludge Sales

There are no updates from the report of December 23, 2010.

## 3 Review Ceased for Technologies

Since the July 2011 update, we have ceased trials with polymeric DTC from Kroff 9011 and Hychem DP4. We continue to evaluate the options for scale and will be reporting as progress is made on the same.

## 4 Polyol waste stream treatment

We have identified our polyol ix waste stream (between 16-22% of total nickel load) as a significant contributor of inorganic nickel due to corrosion of our distillation columns. Initial work using high pH precipitation has shown almost a complete removal of soluble nickel.

Initial work suggests a pH modification would eliminate all soluble nickel from the IX regen streams with chemical costs about █████\$ per day.

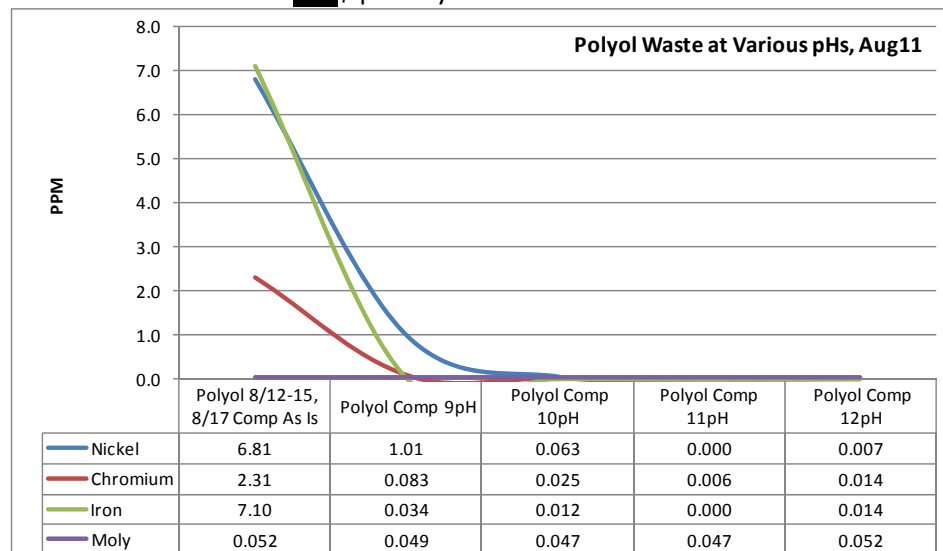


Figure 15: Effect of pH on precipitation on Polyol ion exchange regeneration streams.

Table 5: High pH precipitation of Polyol ion exchange regeneration streams						
				Adjust to 10pH:		
2.5	%NaOH, w/w	Polyol Flows:	lbs / day	lbs 50% NaOH / day		\$ / day
90	sample, ml	8/12/11	61,400	3,014		█████
10.45	g NaOH to 9pH	8/13/11	65,400	3,210		█████
10.6	g NaOH to 10pH	8/14/11	60,730	2,981		█████
10.8	g NaOH to 11pH	8/15/11	119,800	5,880		█████
16.4	g NaOH to 12.2pH	8/17/11	27,940	1,371		█████

06/30/2014 - \* \* \* R2014-024 \* \* \*

\$	50% Caust / lb						
1.6	Starting pH						

The Process Development group at ADM Bioproducts has investigated using gypsum (Table 7) as a filter media and seen nickel reductions over using a 0.1um Filter (Table 6).

Sample (ppm)	Ni	Zn	P
Waste Water Feed	860.32	3.76	0.818
Waste water/NaOH solution	658.897	2.90	0.856
Treated and filtered waste water	0.300	0.015	0.639

**Note:** Feed was a composite of the discharge from the acid-in and slow rinse cycle in a proportion that is representative of the volume of water used in each cycle. Precipitate was passed through a Buchner filter with a 0.1um filter.

Sample Name	Ni	Zn	P	Cr
	mg/kg	mg/kg	mg/kg	mg/kg
Waste water/NaOH solution	689.0	2.66	2.18	245.1
Treated and filtered waste water	81.94	0.705	18.40	23.32

**Note:** Feed was a composite of the discharge from the acid-in and slow rinse cycle in a proportion that is representative of the volume of water used in each cycle. Precipitated feed was fed to a Buchner funnel with CaSO4 as filter media.

06/30/2014 - \* \* \* R2014-024 \* \* \*

## 5 Appendix A Pilot Plant Trials Update

ADM is piloting equipment identified in our July 2011 update. A summary of the present status of the trials is included below.

1. **Alar Corp.** – Removal using diatomaceous earth and RVF.
2. **FRC Systems International, LLC** – Removal of Ni precipitate using DAF pilot.
3. **GE Power & Water** – Removal using Entrapped Air Flotation (EAF) Pilot.
4. **Kroff Engineering** – Removal using One Pass Microfiltration.
5. **Krofta Chemical Company, Inc.** – Removal using Dissolved Air Flotation (DAF) and Sandfloat Pilot.
6. **Nalco** – Removal using Lamella Gravity Settler and Dynasand.

In early November 2011, tests were completed at ALAR Engineering (Mokena, IL), to screen use of Rotary Vacuum Filter (RVF) as separation method. During a two-day test, Hychem and the following day, Nalco, separately tested coagulant and flocculent chemistry for removing precipitated Nickel from ADM DAF effluent. Results are presented in Tables 8 & 9 and Figures 16 & 17.

TABLE 8: Test Results of 100-gallon batch, RVF Filtration at ALAR Engineering. Starting Feed 0.129 ppm Nickel. Metal precipitant: Nalco TX15029SQ, 50ppm, 30 minute residence time.

	Nickel Reduction (%)	Filtrate Ni (ppm)	Coag (ppm)	Floc1 (ppm)	Floc2 (ppm)	Flux (Gal/Hr/ft2)	D.E.
Hychem, Test 1	55.0	.058	300	0.125	0	36	FW-20
Hychem, Test 2	55.8	.057	200	0.125	0	43	FW-20
Nalco, Test 1	50.4	.064	0	0.5	1.0	50	FW-20
Nalco, Test 2	51.2	.063	0	0.5	1.0	65	FW-40

Table 9: Bench scale testing of Nalmet with RVF at Alar Engineering using Nalco Flocculants (8133/8131).				
Sample Volume : 1L				
Sample #	Treatment	DE Filtrate	Ni	
			Turbidity	Total
			Soluble	mg/kg
		NTU	mg/kg	g
0			0.092	0.091
1	50 ppm TX15029SQ (30 min) + 130 ppm Nalco 2 (1 min)+Filtration through 0.9 um (FW20) DE filter	0.5	0.049	0.061
2	50 ppm TX15029SQ (30 min) + 120 ppm 8133 (1 min)+Filtration through 0.9 um (FW20) DE filter	0.3	0.042	0.052
3	50 ppm TX15029SQ (30 min) + 120 ppm 8131 (1 min)+Filtration through 0.9 um (FW20) DE filter	0.2	0.042	0.053
4	50 ppm TX15029SQ (30 min) + 130 ppm Nalco 2 (1 min)+Filtration through 0.5 um (FA 06) DE filter	0.3	0.035	0.053
5	50 ppm TX15029SQ (30 min) + 120 ppm 8133 (1 min)+Filtration through 0.5 um (FA 06) DE filter	0.3	0.050	0.041

1	50 ppm TX15029SQ (30 min) + 120 ppm 8131 (1 min)+Filtration through 0.5 um (FA 06) DE filter	0.3	0.040	0.046
7	120 ppm 8133 (1 min)+50 ppm TX15029SQ (30 min) + Filtration through 0.5 um (FA 06) DE filter	0.3	0.041	0.048
8	120 ppm 8131 (1 min)+50 ppm TX15029SQ (30 min) + Filtration through 0.5 um (FA 06) DE filter	0.3	0.047	0.050

Nickel reductions with RVF equipment have potential as full-scale option and planned testing at Decatur are scheduled of January 2012.

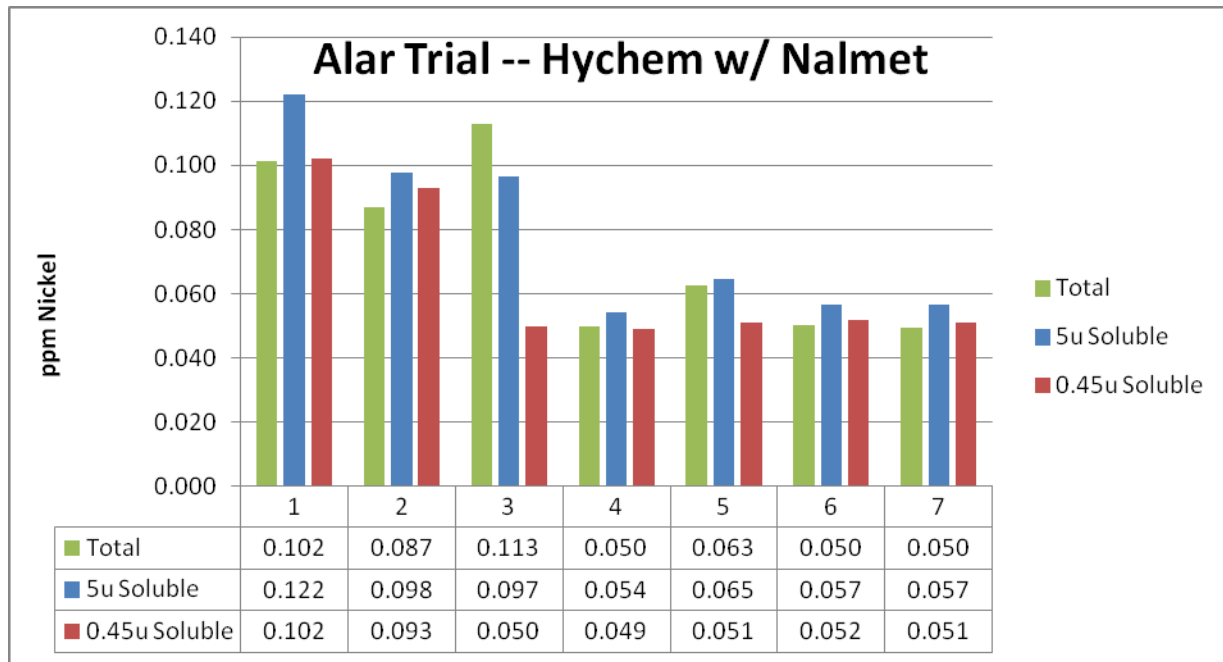
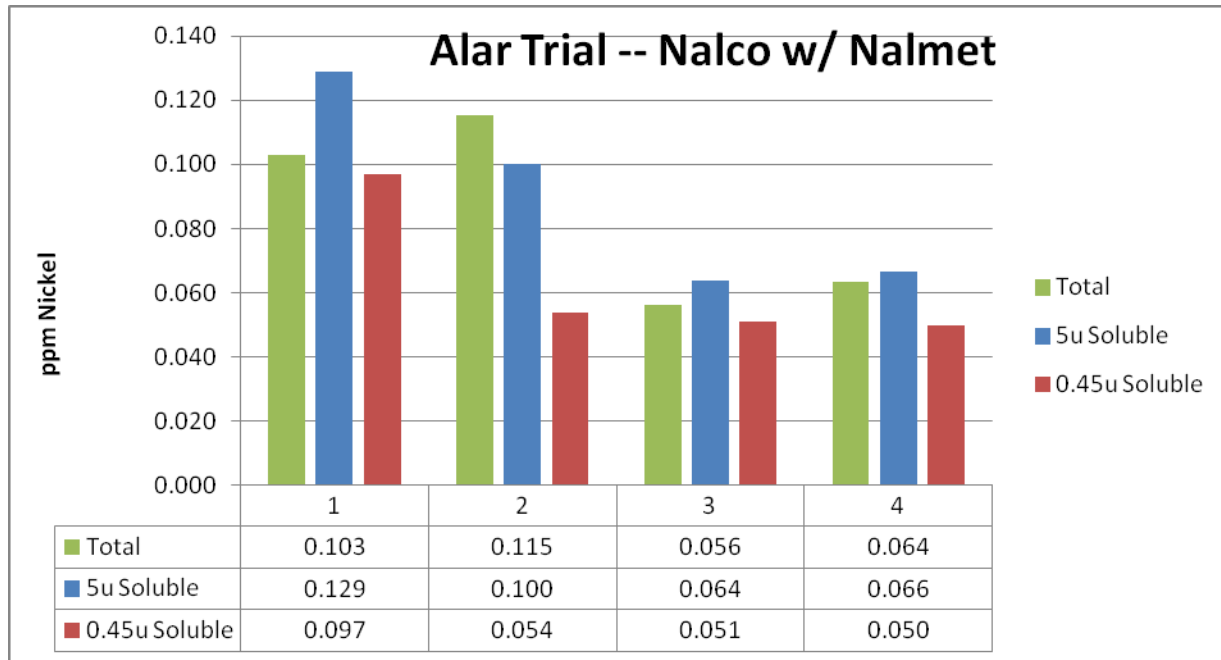


Figure 16: Rotary Vacuum Filtration of Polymeric DTC (Nalco) with Flocculant (Hychem)

06/30/2014 - \* \* \* R2014-024 \* \* \*



**Figure 17: Rotary Vacuum Filtration of Polymeric DTC (Nalco) with Flocculant (Nalco)**

Equipment currently at ADM Decatur Pilot plant:

1. Krofta/Ecolab DAF and Sandfloat pilot.
2. Kroff one-pass microfiltration.

Krofta/Ecolab equipment is ready to begin testing. We have successfully operated equipment at 25 GPM and everything appears to be functional.

Kroff equipment has been tested and filtration rate dramatically slows, filtration flux estimate: 3.2-3.8 Gal/Hr/ft<sup>2</sup>. We have been experiencing technical problems with filtration and are working with the vendor to address them.

FRC Systems International, LLC will be shipping unit to Decatur the week of 05-Dec.





Figure 18: Krofta Sand Filter at ADM pilot plat



Figure 19: Kroff One pass MF at ADM Pilot plant



Figure 20: Alar RVF Filtration with FW40 precoat filteraid

06/30/2014 - \* \* \* R2014-024 \* \* \*

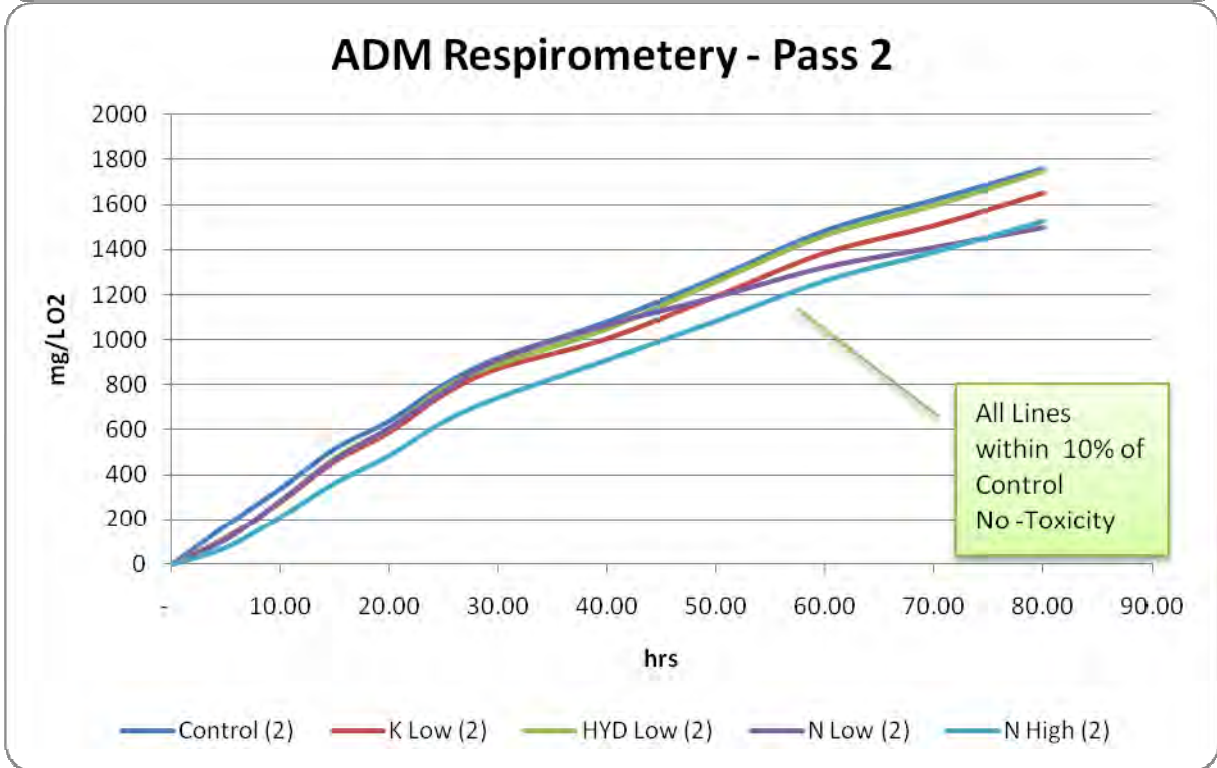
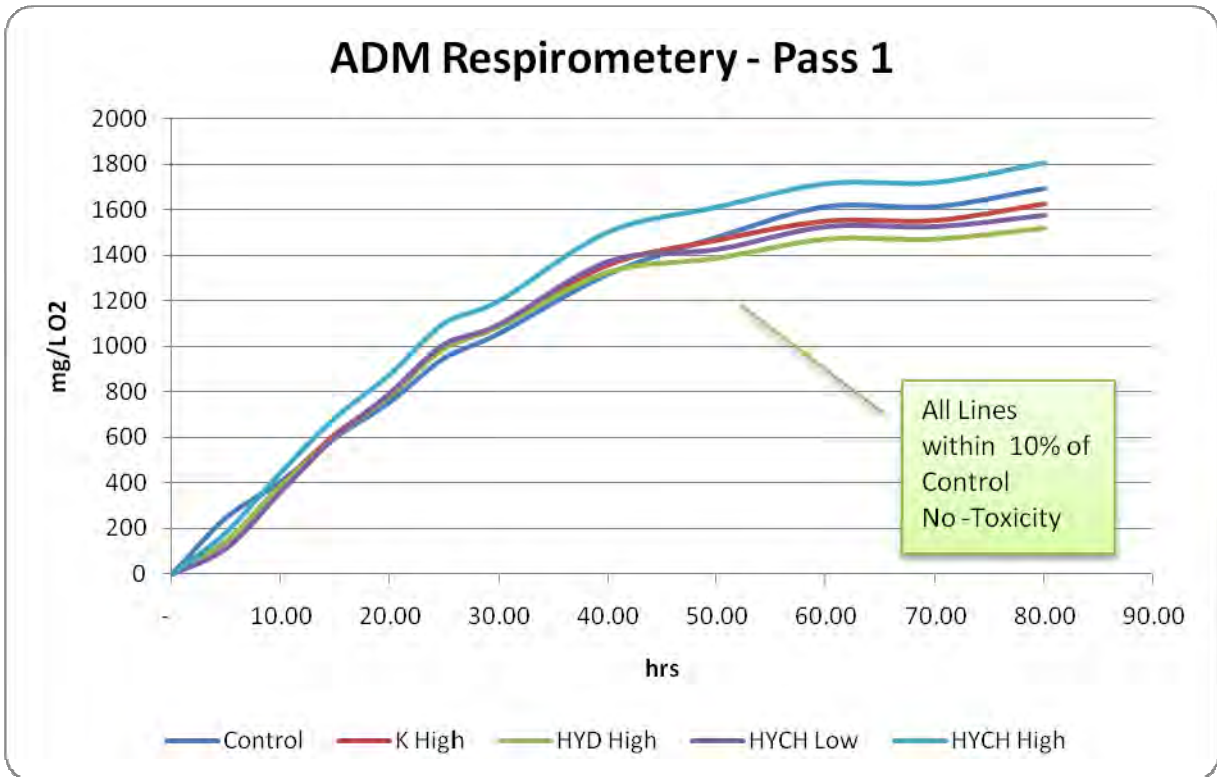
## 6 Appendix B Respirometer and Nitratox Testing

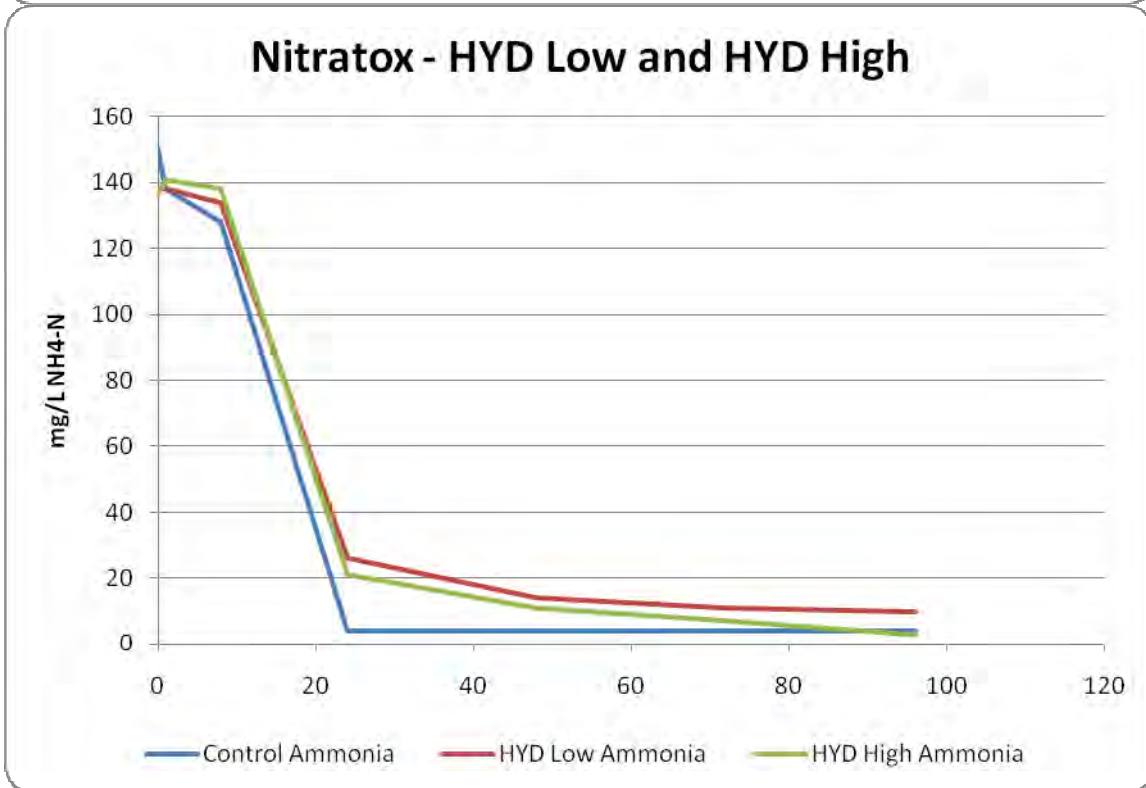
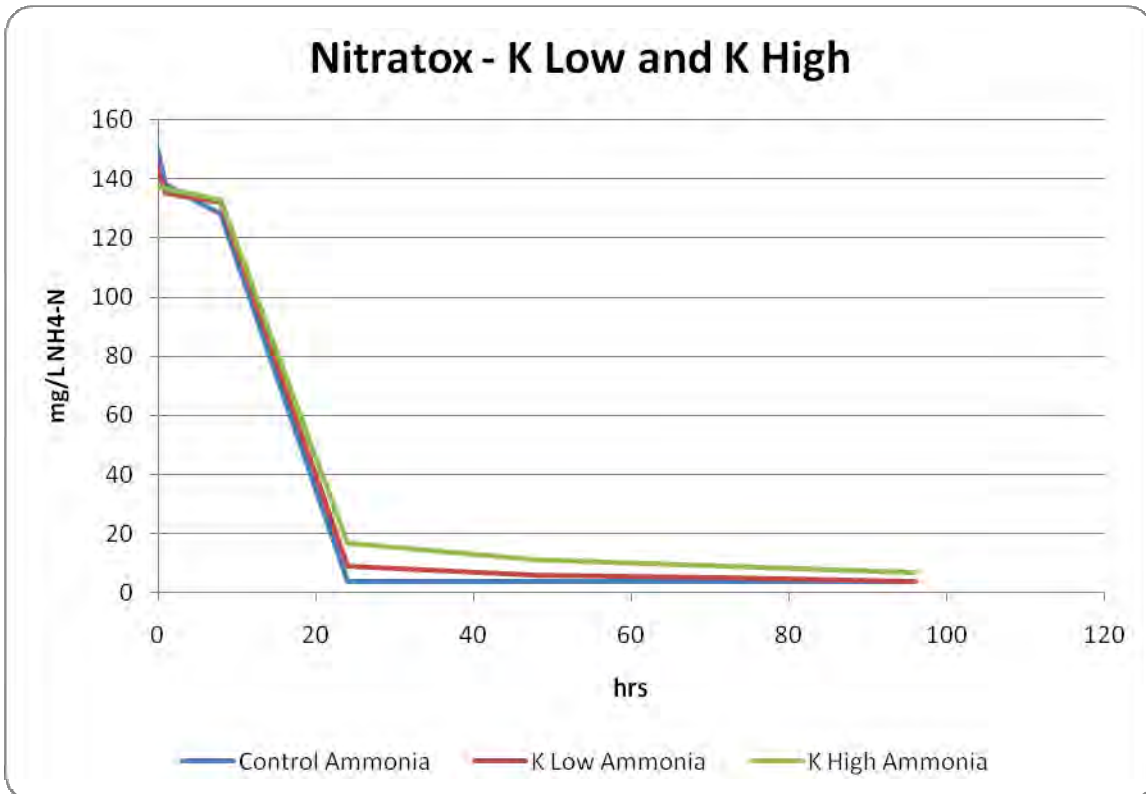
Results from Respirometer and Nitratox testing of Decatur Sanitary Districts MLSS using nickel reduction chemistries piloted at ADM.

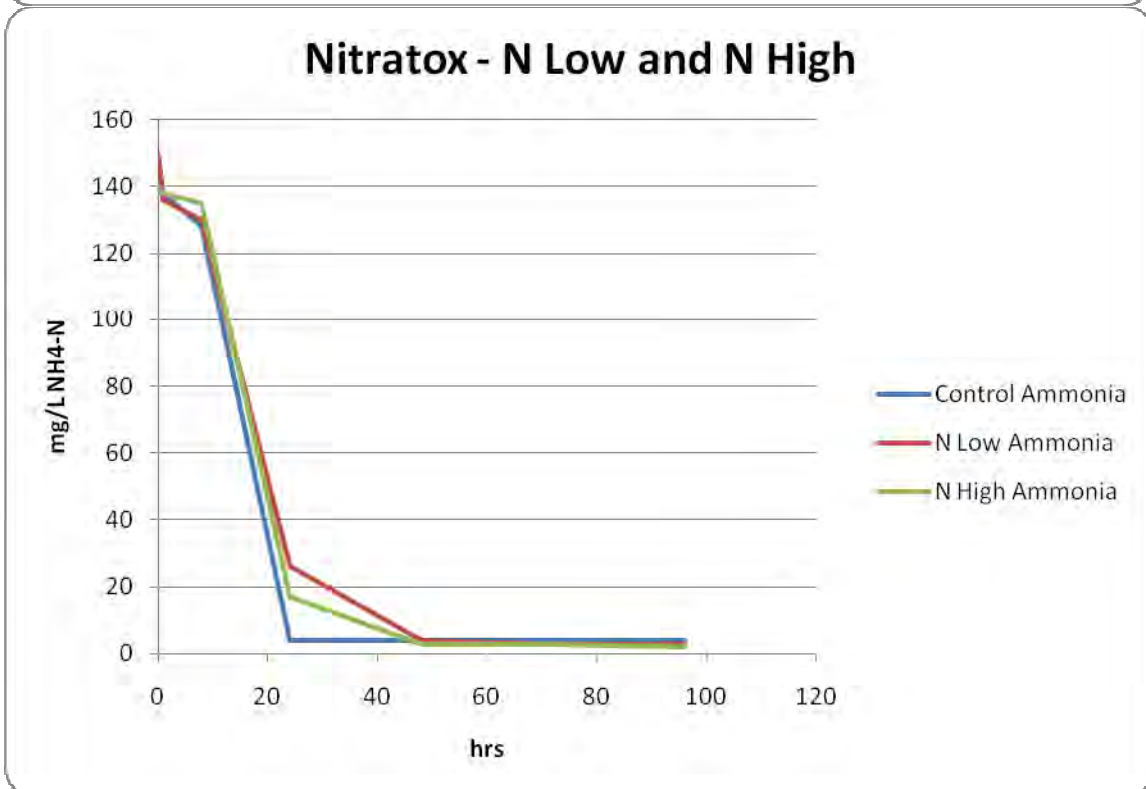
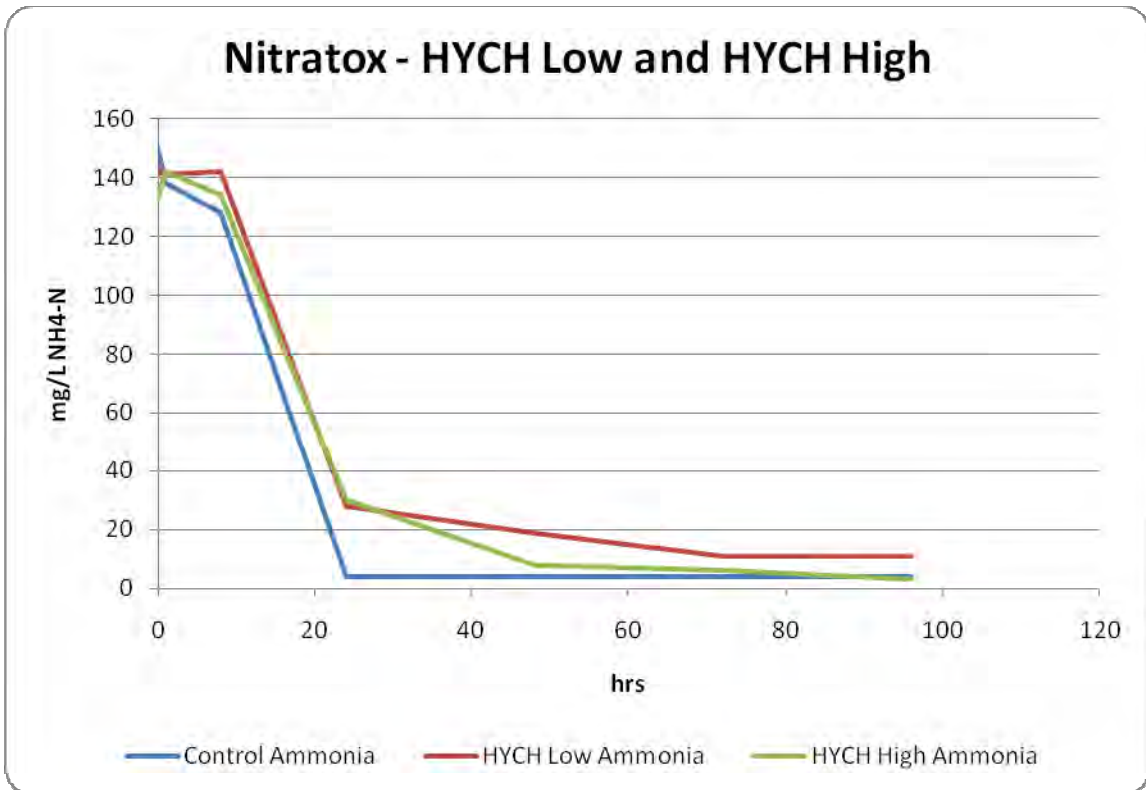
Riverbend Laboratories performed respirometer and Nitratox testing of the four chemistries currently being testing using SDD's MLSS. The chemistries were dosed at ~20ppm and ~200ppm and diluted 50:50 with fresh DAF to simulate a scenario envisioned by the Decatur Sanitary District.

Table 7: Pilot plant results for Samples used for Nitratox and Respirometer testing

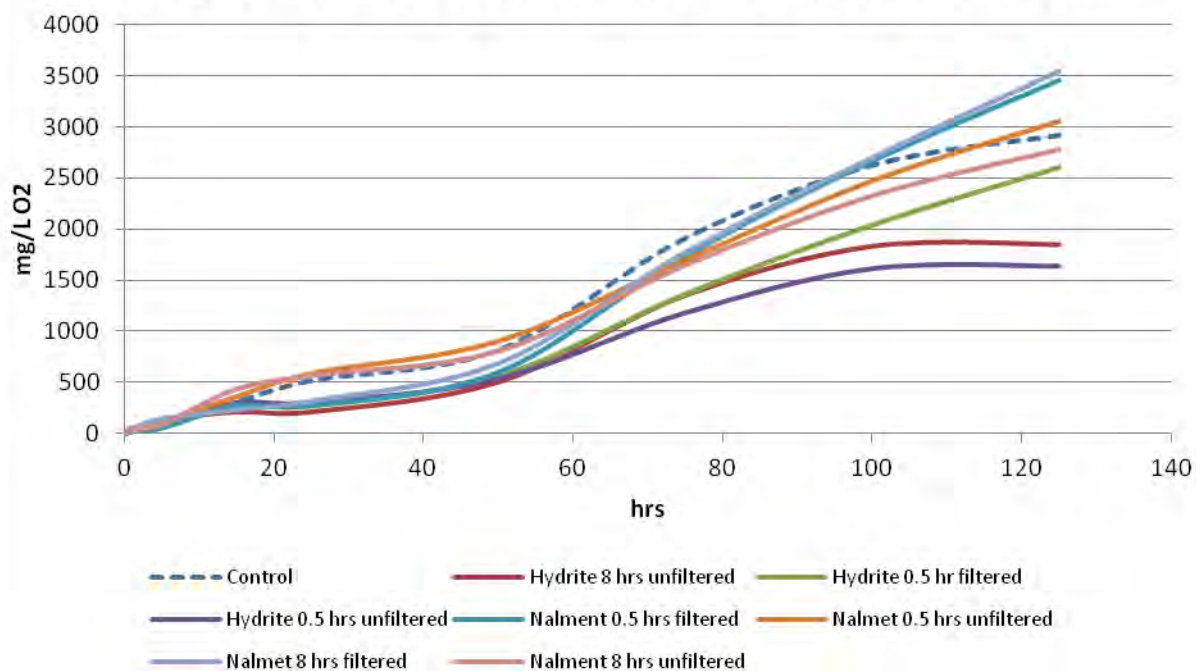
	ppm Nickel	HOLD Time, Hrs	ppm, by wt	% Reduction
LOW SAMPLES TO RIVERBEND			added	
Feed	0.07			
Kroff	0.05	3.75	15.11	0.33
Hydrite	0.04	3.87	18.41	0.34
Hychem	0.06	3.63	18.68	0.18
Nalmet	0.04	3.87	20.39	0.47
HIGH SAMPLES TO RIVERBEND				
02441 5-10 DAF to Pilot DE	0.06			
Kroff	0.02	3.63	190.18	0.58
Hydrite	0.02	3.87	194.07	0.58
Hychem	0.03	3.75	207.83	0.37
Nalmet	0.02	4.23	254.95	0.60



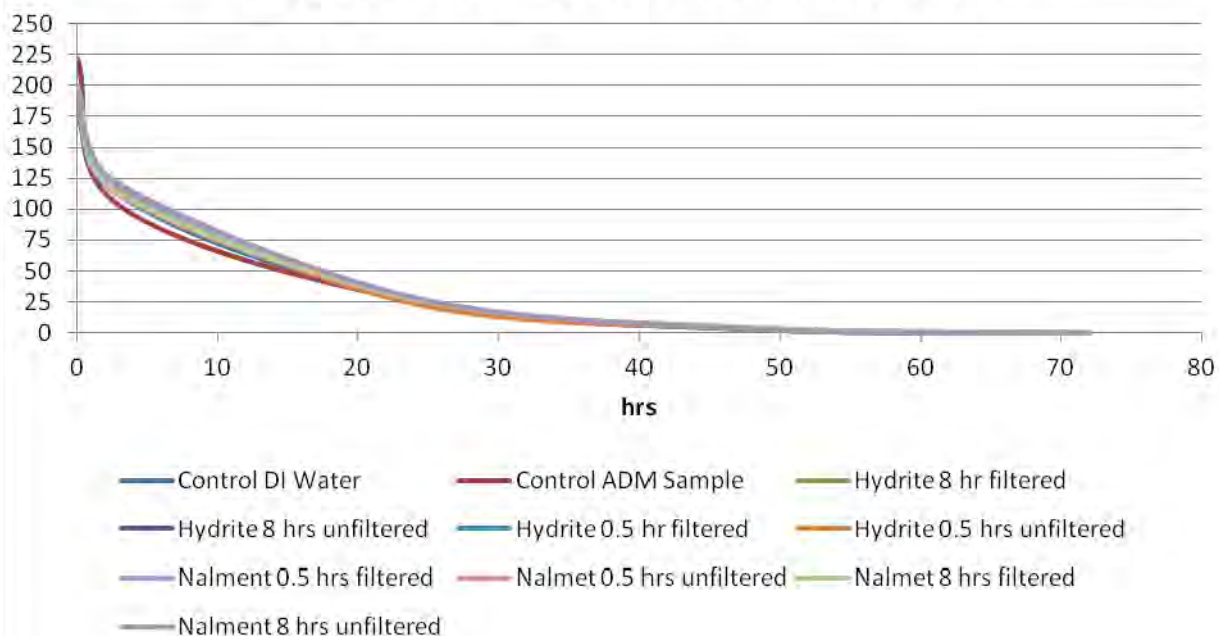




### Respirometry for ADM Nickel Project 10-19-11



### City of Decatur-Nitratox Nickel Project



06/30/2014 - \* \* \* R2014-024 \* \* \*





## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

June 25, 2012

Illinois Environmental Protection Agency  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

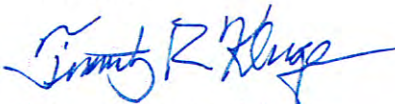
Re: NPDES Permit IL0028321  
IPCB Order PCB 09-125  
Interim Report

Dear Sir or Madam:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 09-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

cc: Rick Pinneo, IEPA (via email)  
Bob Mosher, IEPA (via email)  
SDD File

06/30/2014 - \* \* \* R2014-024 \* \* \*

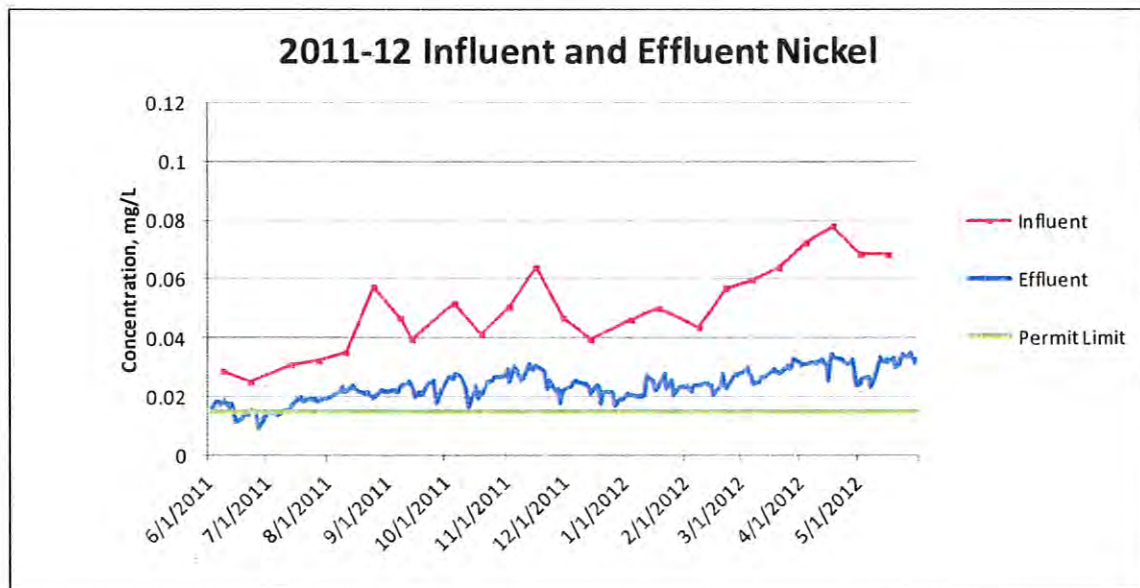
**Sanitary District of Decatur  
Nickel and Zinc Limits  
June 2012 Final Compliance Plan**

The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires the District to achieve compliance with final nickel and zinc effluent limitations by July 1, 2010. This Special Condition also notes that the permit may be modified to include revised compliance dates in Pollution Control Board orders, and that prior to such permit modification, the revised dates in the appropriate orders shall govern the Permittee's compliance.

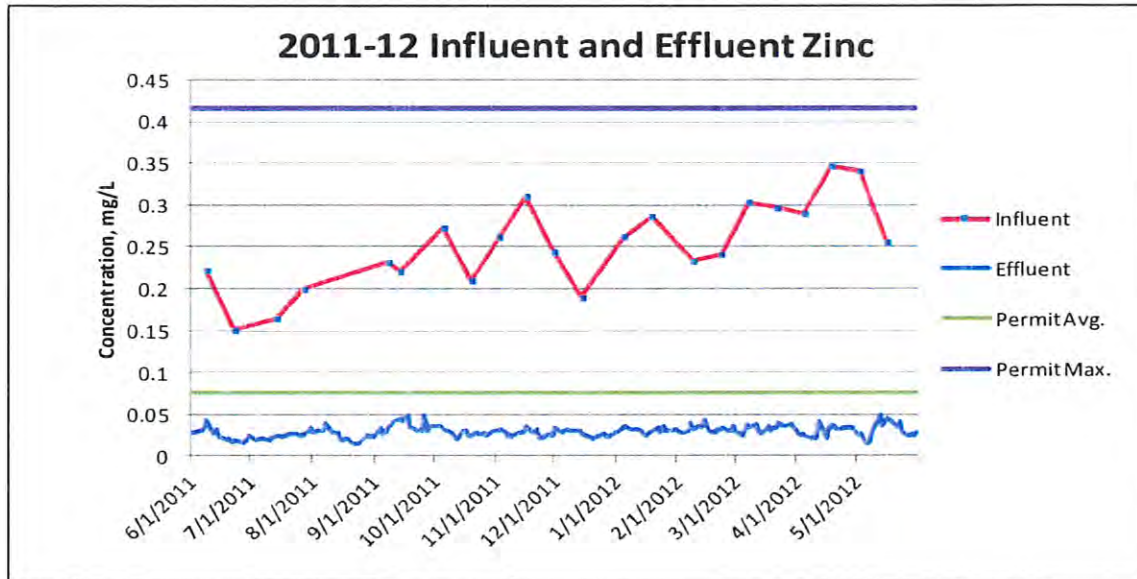
On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified to incorporate the variance although Illinois EPA issued a Public Notice and draft modified permit on May 26, 2011. The Board Order also requires that a final compliance plan be submitted to Illinois EPA by July 1, 2012 "containing nickel and zinc controls, treatment technologies, proposed permit modifications, or proposed site-specific water quality standards that will achieve compliance with the District's NPDES permit effluent limits for nickel and zinc." This report is submitted to meet both the permit and variance requirements.

### Plant Influent and Effluent Sampling

Ongoing influent sampling for nickel and zinc continues at a frequency of twice monthly, and effluent sampling is done five days per week according to NPDES monitoring requirements. A summary of influent and effluent values during the past twelve months is shown below.



06/30/2014 - \* \* \* R2014-024 \* \* \*



Data shows that the plant effluent is not able to consistently meet the current nickel permit limit. Effluent zinc concentrations remain below the permit limit.

### Receiving Stream Sampling

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. One upstream and four downstream sampling sites are being monitored. A summary of 2011-2012 river monitoring data is attached. Downstream nickel results remain high during times of low upstream river flow; low flows have prevailed during most of the past year. All upstream and downstream zinc results during 2011 and 2012 have been below the Illinois water quality standard.

### Pretreatment Ordinance Limits

The District's pretreatment ordinance was amended in October 2009 as noted in previous interim reports.

### Stream Flow-Based Compliance Options

The District continues investigation of flow-based permit limits, to take advantage of upstream flow for mixing when it is available. This concept could potentially allow a savings in treatment facility operating costs when the upstream flow is sufficient to meet water quality standards after mixing with treatment plant effluent. A USGS flow gauging station is located about two miles upstream of the District's discharge point, and provides near- real time flow information. A proposal for flow-based limits will be a part of relief requested from the Pollution Control Board.

06/30/2014 - \* \* \* R2014-024 \* \* \*

### **Water Quality Standard Investigations**

The District is in the final stages of preparing a petition for a site-specific nickel standard, which we expect to file with the Pollution Control Board in in early July 2012.

We are also following the Pollution Control Board rulemaking currently underway to correct an error found in the existing zinc water quality standard. If the Board adopts the corrected standard, utilizing the corrected number to determine our permit limit should provide further assurance of compliance.

### **Industrial Source Sampling and Investigations**

Sampling at Archer Daniel Midland Company for metals continues at a frequency of twice monthly and other industries discharging metals are sampled quarterly. Sample results obtained from ADM within the past two years are attached.

The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits. Final local limits will be determined following Board action on the District's WQS request.

Both ADM and Tate & Lyle formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. District staff met with ADM personnel several times during the first half of 2012. The District's pretreatment permit requires semi-annual reports of ADM's investigations, and the most recent report is attached. Completed and anticipated modifications made by ADM are listed on pages 3-4 of the report.

### **Additional Pretreatment Limit Investigations**

Pretreatment ordinance limits adopted in 2009 were adopted as total (rather than soluble) limits based on review of soluble/insoluble data. Refinement of pretreatment limits is an ongoing process and will depend on final permit limits as well as treatment technologies that might be employed by industrial users.

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Compliance Plan**

District and ADM staff met with Illinois EPA personnel on May 8, 2012 to discuss the District's compliance plan approach. In summary, the District's compliance plan includes the following:

1. Continue to work with ADM to implement nickel discharge reductions and removal technologies. ADM's May 31, 2012 Interim Report describes the completed and planned reductions.
2. Complete and file a petition for a site-specific water quality standard for nickel, based on bioavailability. We anticipate providing a draft of the petition to Illinois EPA before the end of June and filing the petition with the Pollution Control Board in July.
3. The Board petition will contain a request for variable permit limits based on the amount of flow available in the Sangamon River.

Sanitary District of Decatur  
Nickel and Zinc River Data 2010-2011

06/30/2014 - \* \* \* R2014-024 \* \* \*

Sample Date	Plant Final Effluent Nickel mg/L	River Up-stream Nickel mg/L	River 100 yds Down-stream Nickel mg/L	River 600 yds Down-stream Nickel mg/L	Steven's Creek Nickel mg/L	River Rock Springs Bridge Nickel mg/L	River Wyckle's Road Nickel mg/L	Plant Final Effluent Zinc mg/L	River Up-stream Zinc mg/L	River 100 yds Down-stream Zinc mg/L	River 600 yds Down-stream Zinc mg/L	Steven's Creek Zinc mg/L	River Rock Springs Bridge Zinc mg/L	River Wyckle's Road Zinc mg/L	Plant Final Effluent Flow mgd	River Up-stream Flow ft <sup>3</sup> /sec
01/13/11	0.0181	<0.00131	0.00519	0.00495	<0.00131	0.00426	0.00504	0.0503	<0.00660	0.0157	0.0152	<0.00660	0.0133	0.0149	29.48	121
01/27/11	0.0218	<0.00131	0.0144	0.0138	<0.00131	0.0113	0.0102	0.0773	<0.00660	0.0504	0.0481	<0.00660	0.0394	0.0350	30.71	3.9
02/10/11	0.0214	<0.00131	0.0141	0.0128	<0.00131	0.0112	0.00971	0.0701	<0.00660	0.0460	0.0413	0.00761	0.0364	0.0313	27.94	5.4
02/24/11	0.0132	0.00160	0.00242	0.00252	0.00150	0.00214	0.00205	0.0406	0.00841	0.0106	0.0108	0.0138	0.0114	0.00992	44.38	1970
3/10/11	0.0123	0.00169	0.00194	0.00198	0.00153	0.00184	0.00208	0.0321	0.00972	0.00978	0.00992	0.0103	0.00974	0.0100	47.51	2900
3/24/11	0.0132	<0.00131	0.00133	0.00133	<0.00131	<0.00131	<0.00131	0.0161	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	33.28	667
4/7/11	0.0163	<0.00131	0.00343	0.00252	<0.00131	0.00241	0.00237	0.0246	<0.00660	0.00884	0.00689	<0.00660	0.00732	0.00691	30.62	326
4/21/11	0.0118	<0.00131	0.00236	0.00195	0.00254	0.00157	0.00188	0.0215	0.00729	0.00878	0.00822	0.0170	0.00939	0.00934	52.22	2540
5/5/11	0.0147	0.00177	0.00279	0.00238	0.00137	0.00218	0.00223	0.0295	<0.00660	0.00932	0.00862	<0.00660	0.00760	0.00898	41.88	1670
5/19/11	0.0125	<0.00131	0.00211	0.00186	<0.00131	0.00153	0.00150	0.0213	<0.00660	<0.00660	<0.00660	<0.00660	<0.00660	0.00777	32.29	1290
6/9/11	0.0187	<0.00131	0.00143	0.00194	0.00183	0.00162	0.00177	0.0434	<0.00660	<0.00660	0.00672	<0.00660	<0.00660	0.0124	29.12	1540
6/23/11	0.0154	0.00210	0.00335	0.00307	0.00154	0.00280	0.00329	0.0203	0.0131	0.0134	0.0138	0.0112	0.0129	0.0155	36.23	800
7/14/11	0.0170	<0.00131	0.0118	0.0116	<0.00131	0.00886	0.00890	0.0242	0.00519	0.0162	0.0171	<0.00660	0.0136	0.0130	27.12	200
7/28/11	0.0188	<0.00131	0.0187	0.0168	<0.00131	0.0158	0.0159	0.0255	<0.00660	0.0279	0.0219	<0.00660	0.0205	0.0207	27.85	2.1
8/11/11	0.0218	0.00143	0.0255	0.0212	<0.00131	0.0204	0.0199	0.0294	<0.00660	0.0576	0.0292	<0.00660	0.0266	0.0271	24.82	1.6
8/25/11	0.0193	<0.00131	0.0187	0.0190	<0.00131	0.0183	0.0189	0.0161	<0.00660	0.0153	0.0158	<0.00660	0.0142	0.0137	24.19	1.1
9/8/11	0.0233	0.00142	0.0208	0.0222	<0.00131	0.0207	0.0196	0.0341	<0.00660	0.0294	0.0303	<0.00660	0.0279	0.0254	27.07	0.15
9/14/11	0.0237	0.00132	0.0231	0.0235	<0.00131	0.0228	0.0231	0.0460	<0.00660	0.0425	0.0438	<0.00660	0.0413	0.0385	28.62	1.9
10/6/11	0.0276	0.00140	0.0263	0.0265	<0.00131	0.0255	0.0259	0.0329	<0.00660	0.0318	0.0314	<0.00660	0.0296	0.0288	23.96	0.75
10/20/11	0.0211	<0.00131	0.0189	0.0195	<0.00131	0.0159	0.0181	0.0260	0.0107	0.0235	0.0238	<0.00660	0.0193	0.0199	23.28	2.8
11/3/11	0.0250	0.00197	0.0277	0.0304	0.00175	0.0260	0.0275	0.0322	0.0115	0.0314	0.0354	<0.00660	0.0281	0.0271	42.99	18
11/17/11	0.0307	<0.00131	0.0281	0.0283	0.00178	0.0273	0.0277	0.0368	<0.00660	0.0285	0.0304	<0.00660	0.0275	0.0247	25.80	1.1
12/1/11	0.0221	<0.00131	0.0177	0.0173	<0.00131	0.0149	0.0149	0.0349	0.00728	0.0245	0.0230	0.00824	0.0207	0.0190	27.64	2.1
1/5/12	0.0207	<0.00131	0.0193	0.0206	<0.00131	0.0170	0.0174	0.0355	<0.00660	0.0328	0.0346	<0.00660	0.0298	0.0278	27.19	4.1
1/19/12	0.0245	0.00146	0.0164	0.0166	0.00135	0.0126	0.0127	0.0307	0.0265	0.0229	0.0240	0.00838	0.0203	0.0184	26.24	8.9
2/9/12	0.0241	<0.00131	0.00567	0.00496	<0.00131	0.00480	0.00421	0.0329	<0.00660	0.00944	0.00838	<0.00660	0.00788	0.00782	29.94	228
2/23/12	0.0227	<0.00131	0.0135	0.0147	<0.00131	0.0118	0.0115	0.0343	<0.00660	0.0213	0.0256	<0.00660	0.0182	0.0172	28.01	50
3/8/12	0.0245	<0.00131	0.0111	0.0111	<0.00131	0.00964	0.00941	0.0338	<0.00660	0.0167	0.0161	<0.00660	0.0149	0.0150	27.78	79
3/22/12	0.0277	<0.00131	0.0241	0.0211	<0.00131	0.0180	0.0185	0.0399	<0.00660	0.0501	0.0387	<0.00660	0.0245	0.0227	26.74	2.5
4/5/12	0.0313	<0.00131	0.0226	0.0226	<0.00131	0.0205	0.0207	0.0260	<0.00660	0.0214	0.0227	<0.00660	0.0185	0.0172	26.05	4.6
4/19/12	0.0334	<0.00131	0.0246	0.0238	0.00149	0.0187	0.0199	0.0375	<0.00660	0.0331	0.0308	<0.00660	0.0240	0.0216	26.08	4.2
5/3/12	0.0262	0.00158	0.0120	0.0105	<0.00131	0.00755	0.00770	0.0270	0.00690	0.0231	0.0194	<0.00660	0.0148	0.0142	26.95	8.7
5/17/12	0.0317	0.00156	0.00859	0.00888	0.00141	0.00775	0.00806	0.0450	<0.00660	0.0160	0.0171	<0.00660	0.0139	0.0148	25.37	97

Indicates that effluent or river/creek sample concentration exceeds chronic water quality value

06/30/2014 - \* \* \* R2014-024 \* \* \*

SDD Major Industrial Nickel and Zinc Results				
	ADM Point A	ADM Point A	ADM Point D	ADM Point D
Sample	Nickel, Tot	Zinc, Tot	Nickel, Tot	Zinc, Tot
Date	mg/L	mg/L	mg/L	mg/L
6/1/2010	0.0813	0.488	0.12	0.441
6/14/2010	0.0826	0.453	0.104	0.345
7/8/2010	0.148	0.54	0.283	1.07
7/12/2010	0.144	0.528	0.193	0.514
8/2/2010	0.125	0.457	0.172	0.446
8/9/2010	0.126	0.44	0.184	0.474
9/1/2010	0.0766	0.465	0.122	0.469
9/20/2010	0.0744	0.442	0.121	0.649
10/4/2010	0.0781	0.461	0.0938	0.369
10/14/2010	0.162	1.18	0.179	1.18
11/8/2010	0.0524	0.24	0.0646	0.208
11/23/2010	0.13	0.665	0.122	0.413
12/6/2010	0.0715	0.53	0.131	0.581
12/13/2010	0.0649	0.498	0.0774	0.219
1/5/2011	0.0629	0.53	0.0669	0.204
1/10/2011	0.0577	0.495	0.0666	0.188
2/7/2011	0.0836	0.756	0.0892	0.329
2/14/2011	0.0589	0.472	0.0598	0.18
3/7/2011	0.0773	0.447	0.0627	0.128
3/14/2011	0.086	0.51	0.1	0.449
4/4/2011	0.07	0.428	0.0841	0.387
4/20/2011	0.0687	0.33	0.0861	0.347
5/2/2011	0.0712	0.304	0.0809	0.302
5/9/2011	0.06	0.301	0.0712	0.3
6/6/2011	0.0648	0.285	0.0786	0.276
6/13/2011	0.0692	0.293	0.0809	0.314
7/11/2011	0.0542	0.226	0.0625	0.209
8/1/2011	0.0491	0.165	0.0621	0.172
8/8/2011	0.0567	0.215	0.074	0.242
9/1/2011	0.0662	0.285	0.0842	0.327
9/7/2011	0.0684	0.311	0.0884	0.344
10/3/2011	0.094	0.518	0.114	0.515
10/10/2011	0.0643	0.191	0.073	0.189
11/7/2011	0.0912	0.377	0.116	0.529
11/22/2011	0.221	1.28	0.136	0.623
12/1/2011	0.0917	0.416	0.11	0.492
12/5/2011	0.094	0.423	0.117	0.508
1/5/2012	0.0921	0.451	0.111	0.531
1/9/2012	0.0868	0.424	0.109	0.491
2/6/2012	0.121	0.441	0.134	0.488
2/13/2012	0.127	0.49	0.159	0.601
3/5/2012	0.128	0.431	0.15	0.493
3/12/2012	0.12	0.406	0.141	0.482
4/12/2012	0.169	0.621	0.191	0.705
4/19/2012	0.148	0.516	0.176	0.674
SDD Ordinance Limit (Avg.)	0.0365	0.45		
SDD Ordinance Limit (Max.)	0.15	1.7		

06/30/2014 - \* \* \* R2014-024 \* \* \*



RECEIVED

JUN 04 2012

SANITARY DISTRICT  
OF DECATUR

May 31, 2012

CERTIFIED MAIL  
7003 3110 0005 2739 4722

Charles Jarvis  
Pretreatment Coordinator  
Sanitary District of Decatur  
501 Dipper Lane  
Decatur, Illinois 62522

Re: Interim Nickel and Zinc Report, 2012-1

Dear Charles,

Per Special Condition E.8. of the ADM Industrial Discharge Permit #200, ADM is enclosing the semi-annual report that summarizes ADM's research efforts to reduce nickel and zinc from effluent during the first half of CY2012. In Tables 1 & 2 of the report you will note that we have struck reference to any vendors associated with technology studies. This is in accordance with confidentiality agreements in place with those vendors.

Please contact our Environmental Manager Mark Atkinson if you have any questions or would like to arrange a meeting to discuss.

Regards,

A handwritten signature in black ink that reads 'Mark Burau'. The signature is fluid and cursive, with the first name 'Mark' and last name 'Burau' clearly legible.

Mark Burau  
Plant Manager  
ADM Decatur Corn Processing Plant

Ec: Mark Atkinson – ADM Corn Plant Environmental Manager  
Dean Frommelt – ADM Corn Division Environmental Manager  
EDMS



06/30/2014 - \* \* \* R2014-024 \* \* \*

To: Illinois Environmental Protection Agency  
Decatur Sanitary District

From: ADM Decatur WWTP

CC: ADM Corn Processing, ADM Oilseeds Processing, ADM JRRRC

Date: May 31, 2012

Re: Status Report Compliance Strategy for 2012 for Decatur Sanitary District and ADM  
Decatur WWTP for waste treatment. (Covers updates post December, 2011- date)



**Table of Contents**

Table of Contents ..... 1

1 Background..... 3

2 Reduction in total and soluble nickel between ADM Discharge and SDD effluent..... 16

3 Corn Plant used IX system ..... 17

4 Review Ceased for Technologies ..... 19

5 Polyol waste stream treatment..... 19

6 Appendix A Respirometer and Nitratox Testing..... 22

06/30/2014 - \* \* \* R2014-024 \* \* \*

ADM Research and Decatur Corn Processing have been actively pursuing technologies to remove Nickel (Ni) from its effluent stream released to the SDD treatment plant. Enclosed is a report on the progress ADM has made since the last update issued on December 2011.

#### **1 Background and Update (post December 2011)**

Nickel and Zinc are present in effluent leaving the ADM Decatur Complex Waste Water plant. Of the two metals, nickel is more difficult to remove from the effluent. ADM has conducted 5 plant material balances to understand the sources of Nickel in its internal streams. ADM's Decatur Complex consists of multiple, separate processing plants, which send their wastewater to the on-site wastewater treatment plant ("WWTP") operated by Corn Plant personnel. These processing plants consist of the Corn Wet Mill, BioProducts Plant, Cogeneration Plant, East Soybean Processing Plant, West Soybean Processing Plant, Vitamin E Plant, Corn Germ Processing Plant, Glycols Plant and the Polyols Plant. Each of these unique plants produces multiple products, using both batch and continuous processes, and creates water streams which generally are reused multiple times prior to being discharged to the WWTP. The WWTP treats approximately 11 MGD through a newer anaerobic treatment system followed by aerobic treatment prior to discharge to the District.

The incoming soybeans contain approximately 4.1 parts per million ("ppm") nickels, while incoming corn contains approximately 0.53 ppm nickel. Given that ADM's Decatur Complex processes approximately 600,000 bushels of corn and 200,000 bushels of soybeans per day, our incoming Nickel load are about 49.2 lbs from the Soybeans and 19.1 lbs from the corn. A small portion of the incoming nickel is discharged in the effluent.

In ADM effluent water originates in the corn and soybeans being processed at the facility. During the processing, the metals are released and enter the processing water some of which eventually ends up at the wastewater treatment plant.

ADM has monitored soluble Nickel at the Damon and Front stations continuously (see [Figures 1-3](#)) and made a number of modifications in its operations:

- 1) In the past 9 months there has been a decline in Nickel from about 0.120ppm to about 0.060 ppm. However we have experienced severe spikes in effluent nickel in September-November, 2011 each lasting 2-3 days.

06/30/2014 - \* \* \* R2014-024 \* \* \*

- 2) Spent catalyst from the West Soybean Processing Plant is collected and sent to a landfill. Spilled catalyst is collected and disposed of as solid waste rather than washed into a sump.
- 3) Particulate catalyst from the Corn Plant Sorbitol production is captured by filters and physically recovered for recycling or disposal as solid waste. ADM is also installing an ion exchange resin system at the Sorbitol Plant to capture soluble nickel from wastewater.
- 4) The East Soybean Processing Plant is finalizing its design of a system that will remove the soy molasses stream (containing approximately 2.4 lb/day, approximately 35% of the soluble nickel from the Decatur Complex) from the WWTP. This stream is high in digestible, fermentable sugars but will need to be concentrated for stability. The East Soybean Processing Plant has prepared a cost estimate for this process change. Once the system design is complete and the cost estimate approved, ADM anticipates spending several million dollars to install it.
- 5) The Polyols Plant accounts for approximately 11% of the soluble nickel from the Decatur Complex. The Polyols Plant has determined that this nickel can be precipitated by pH adjustment. ADM is now determining how to implement this change on its process stream.
- 6) We have also collected soluble nickel data for the past 8+ yrs. and it shows that our soluble nickel number remain unchanged with the only change in total nickel due to startup of the anaerobic digesters post August 2008.

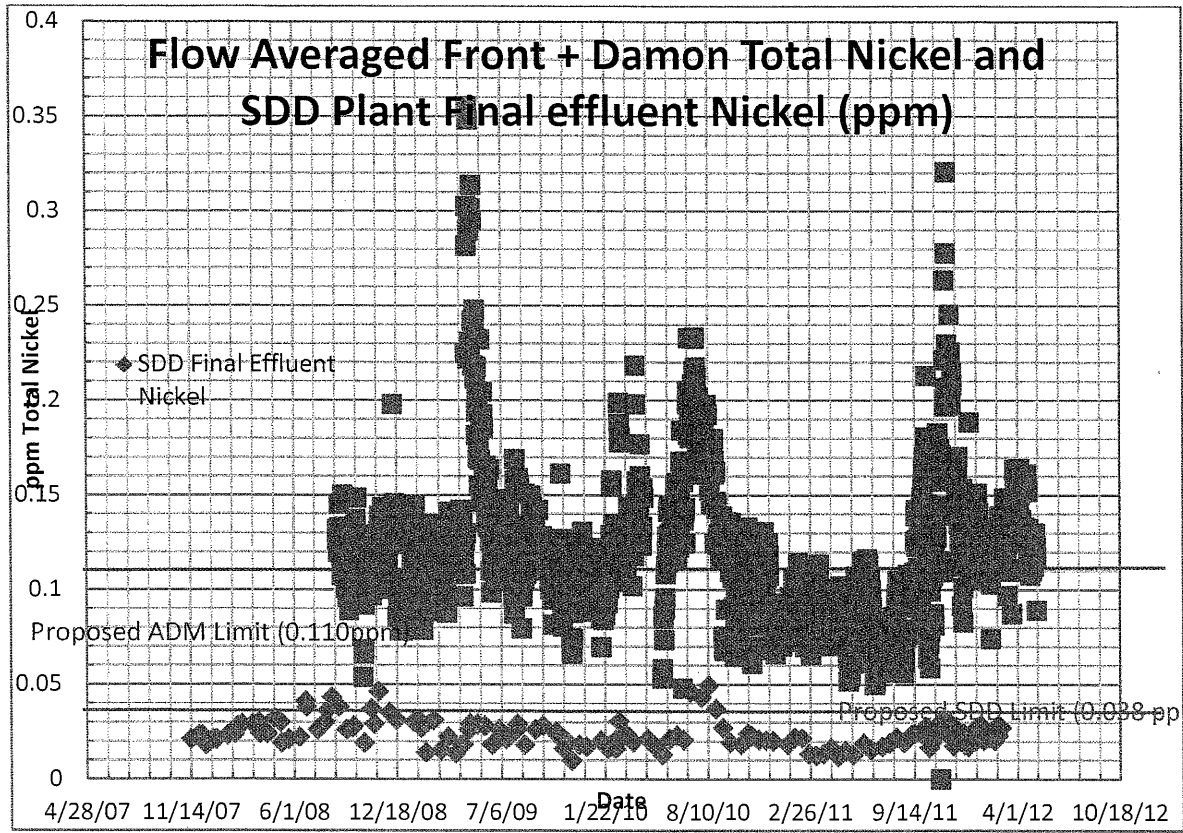


Figure 1 Flow Averaged Front and Damon Nickel

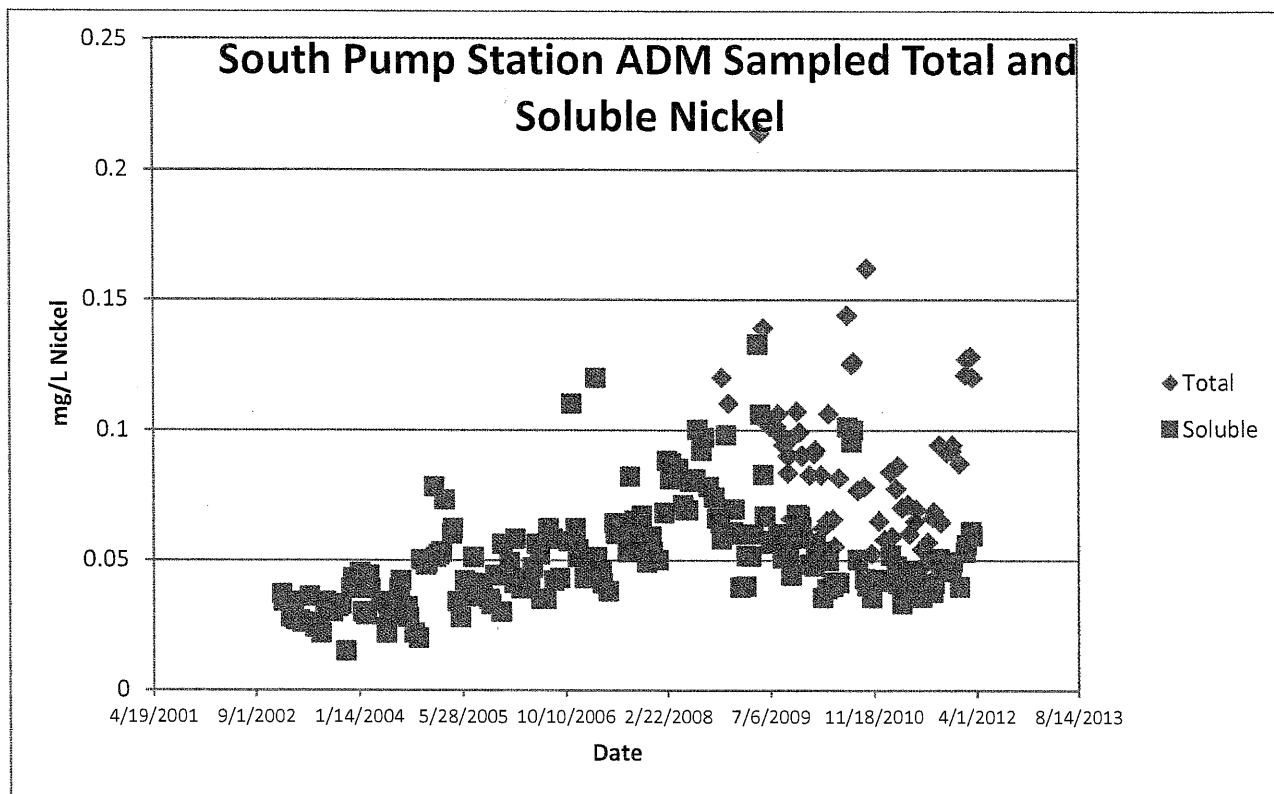


Figure 2 South Pump Station Nickel

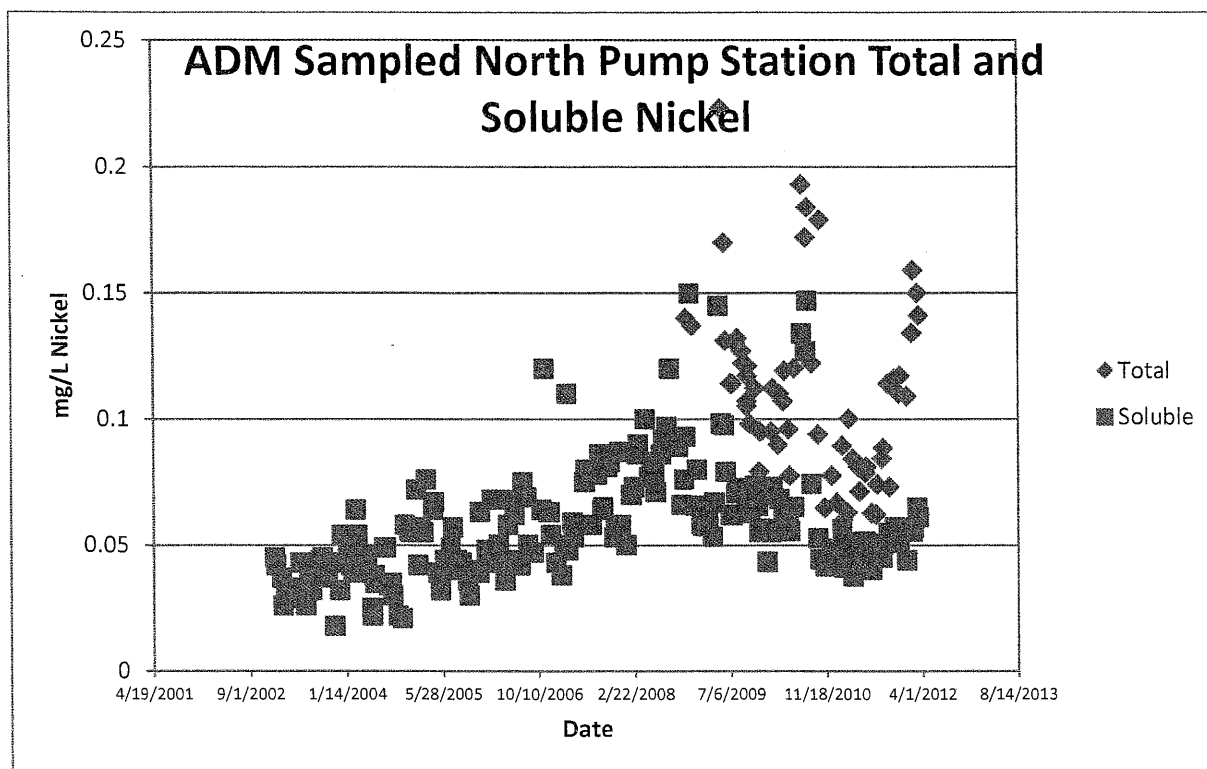


Figure 3 North Pump Station Nickel

06/30/2014 - \* \* \* R2014-024 \* \* \*

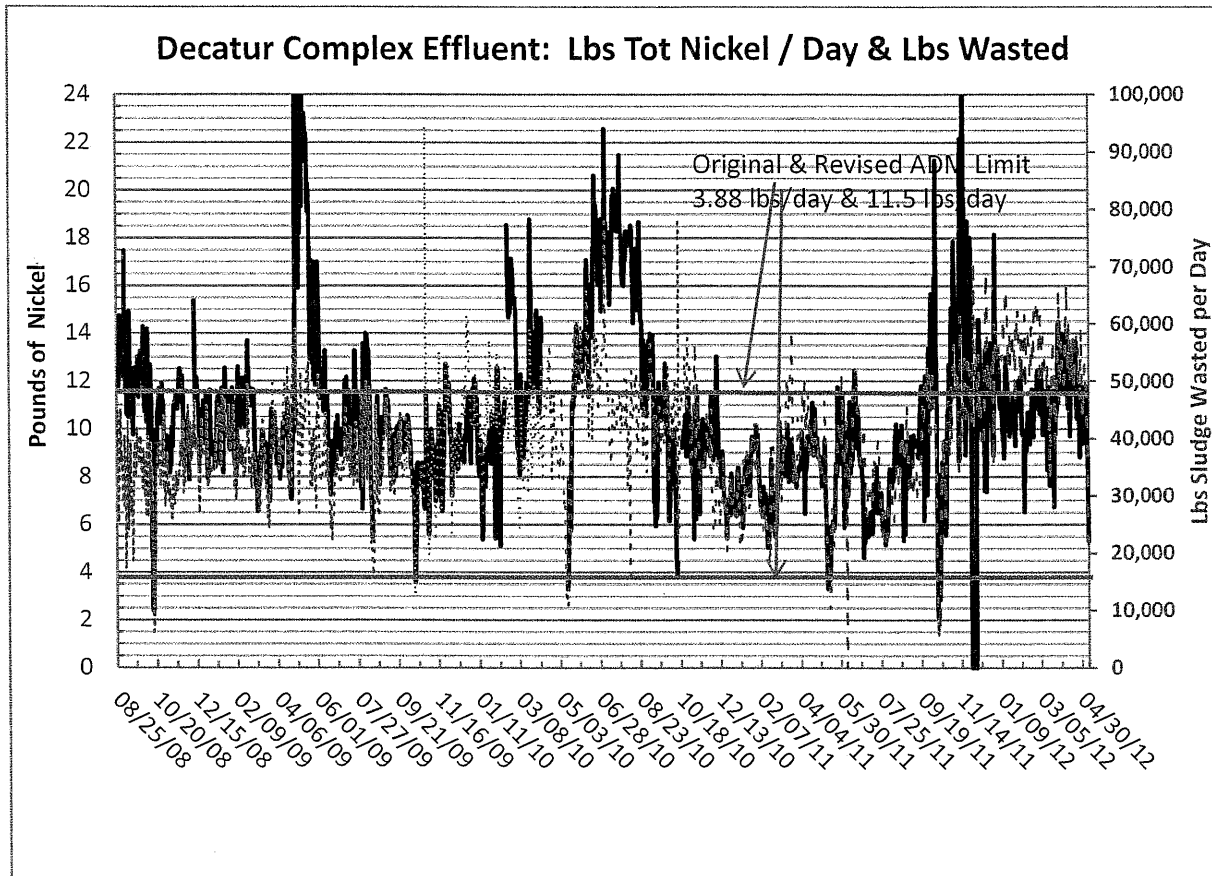


Figure 4 Sludge wasting and Total Nickel ADM WWTP

As reported in the 2010 and 2011 updates, ADM has, thus far, investigated 44 technologies that had the potential to control nickel at the Decatur Complex WWTP. (This was in addition to the work ADM has undertaken to reduce nickel within the individual wastewater streams.) As indicated in [Table 1](#), these technologies can be segregated into six broad categories:

1. Nickel Proprietary Precipitation Process;
2. Nickel Chemical Precipitation;
3. Ion Exchange Resin;
4. Filtration;
5. pH Modification
6. Noncommercial, Experimental Technologies.



06/30/2014 - \* \* \* R2014-024 \* \* \*

Additional details about some of the technologies identified in [Table 1](#) are presented in [Table 2](#), including a general list of reasons why certain of those technologies are not technically feasible and are not currently being pursued.

While most of the technologies evaluated were not found to be technically feasible, ADM identified one technology it had not already actively pursued that it will continue pursuing to reduce nickel at its Polyols Plant. In particular, ADM investigated a technology using pH modification for precipitation of nickel as a hydroxide. During its evaluation, ADM determined that the inorganic nickel present in the effluent leaving the Polyols Plant (which averages about 40,000 gallons per day out of the 11 million gals per day (MGD) Decatur Complex flow) can be precipitated using this technique. However, the majority of nickel present in the bulk of waste streams evaluated appears to be in the form of chelated nickel, which requires a pH swing from 7.0 to 10.0 to 3.0 and back to 7.0. Thus, while pH modification has been determined to be technically feasible to reduce nickel from the Polyols Plant's effluent, the results show that there is still much work to be done to understand and manage the anticipated swings in pH for the entire Decatur Complex. Nevertheless, ADM is committed to determining how to implement this change on the Polyols Plant process stream. It is important to note that, due to the high volume of acid and base that will be required for changing the pH of the waste streams, this approach was not pursued for the dissolved air flotation ("DAF") where the daily volume averages 11.5 MGD effluent, as compared to 0.037 MGD for the Polyols Plant. It is also important to note that, although determined not to be technically feasible, ADM continues to trial polymeric dimethyl dithiocarbamate for use in ADM's final wastewater effluent. This technology would consist of a polymeric dimethyl dithiocarbamate addition to precipitate soluble nickel followed by coagulation and filtration to remove the solid nickel polymer complex. To date, ADM has had reasonable success in some trials with removing 40-60% of the soluble nickel present in DAF effluent water. However, there are still a number of significant technical obstacles to employing this nickel reduction technology, such as scaling, residence time, chemical usage, and nickel reduction percentage and consistency. Further, even if the obstacles inherent in this technology could be overcome, ADM believes that it will continue to be cost prohibitive to employ. [Table 3](#), summarizes the capital, operating and chemical costs for the approaches it is scaling and either installing or continuing to trial.

Thus, of all of the technologies investigated by ADM to date, the only viable option that has not already been fully planned, installed or employed by ADM is the nickel capture process based upon high pH precipitation at the Polyols Plant. Because such technology has been determined to be both

technically feasible and economically reasonable for the specific application, ADM will install that system at the Polyols Plant after necessary pilot testing is complete. However, that reduction, even when combined with the other reductions achieved by ADM, will still not reduce nickel to the levels sought by the District under its current permit. Even if ADM could overcome the technical obstacles it faces regarding the use of polymeric dimethyl dithiocarbamate to reduce nickel from the final wastewater effluent, testing indicates that residual soluble nickel concentrations close to 0.050 mg/L will remain irrespective of contact time and incoming nickel levels. ADM's investment to date to identify and implement viable solutions to meet the nickel standard has been approximately \$1.02 million in employee costs and \$0.45 million in equipment rental and pilot trial costs from 2009 to December 2011. In addition, ADM has spent \$0.45 million to install a resin capture system at the Decatur Sorbitol plant. It is also preparing to spend an additional \$2.5 million to install a system to allow removal of the soy molasses stream and roughly \$0.75 million to install a high pH precipitation and filtration process at the Polyols Plant. ADM has also significantly improved housekeeping in the West Plant to minimize nickel catalyst from entering the wastewater system. Finally, ADM continues to investigate the ability to scale up a potentially viable chemical technology for installation at the Decatur Complex WWTP based on polymeric dimethyl dithiocarbamate to reduce nickel from its effluent. At this point, all reasonably identifiable options have been explored and all technically feasible and economically reasonable solutions are being pursued


Table 1 Summary of Technologies Reviewed by ADM							
	Chemistry	Dosage	Nickel Reduction (%)	Current Status	Nitratox/ Respirom eter Testing*	Technically Feasible (y/n)	Economically Reasonable (y/n)
<b>Category 1 - Nickel Proprietary Precipitation Process</b>							
		1%-3% by weight of clay	40%-60% (from 200ppb influent)	Not Active, High dosages unscalable.	Not tested.	No	No
	Acidic Clay	4%-8% w/w	40% (from 90ppb influent)	Stopped. High dosage.	Not tested.	No	No
	Chitosan Based	5% w/w	90% from 200 ppb influent	Abandoned. High dosage,	Not	No	No

06/30/2014 - \* \* \* R2014-024 \* \* \*











[REDACTED]				Concerns with Chitosan Availability	tested.		
[REDACTED]	Proprietary	2% w/w	82% (from 100ppb)	Abandoned. Company went out of business	Not tested.	No	No
[REDACTED]	Metclear	200 ppm	64% (from 120ppb)	Shelved. Strong pH swing (acidification to pH 2, alkalination to 10 and neutralization)	Not tested.	No	No
[REDACTED]	Not disclosed	Not disclosed	40-60% (from 200ppb)	Shelved. Company not sharing samples.	Not tested.	No	No
<b>Category 2 - Nickel Chemical Precipitation Process Using Carbamates or Organic Sulfides</b>							
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	100ppm with 50ppm of CaCl2	30% from 150ppb	Piloted. Total Nickel reduction to 60ppb.	Passed	No	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	20-50ppm	60% from 150ppb	Piloted. Total Nickel reduction to 54 ppb.	Passed	Yes	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	100ppm	41% from 150ppb	Piloted. Total Nickel reduction to 32ppb	Passed	Yes	No
[REDACTED]	Dimethyl Dithiocarbamate	50ppm + pH 6.0	76% from 150ppb	Piloted. Nickel reduction seen to 40ppb	Passed	Yes	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	300ppm + pH swing	30%	Not active. Modified chemistry from Nalco being tested	Not tested.	No	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	50ppm	48% from 100ppb	Piloted. Nickel reduction seen to 20ppb	Passed	Yes	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	200ppm	52% from 150ppb	Piloted. Nickel reduction seen to 39 ppb	Passed	No	No
[REDACTED]	Polymeric Dimethyl Dithiocarbamate	100ppm	40% from 150ppb	Not piloted. GE has not scaled up commercial manufacturing.	Not tested.	No	No
[REDACTED]	Dimethyl Dithiocarbamate	100ppm	60% from 150ppb	Piloted. Nickel reduction seen to 24 ppb	Passed	No	No
<b>Category 3 - Non Functional Resins</b>							
[REDACTED]	Styrene Divinyl Benzene	2-5% w/w	20%	Not scaled. High regeneration costs	Not tested	No	No

06/30/2014 - \* \* \* R2014-024 \* \* \*

████	Styrene Divinyl Benzene	4% w/w	60%	Not scaled. Very high resin use. Caustic /ethanol based regeneration	Not tested	No	No
████	Immobilized Ion Exchange Beads	5%	Not significant	Shelved	Not tested	No	No
<b>Category 4 - Reuse of Ion Exchange Resin</b>							
████ ████ ████	Sulfonic	0.1-0.5%	Complete removal of Ionic Nickel from the Sorbitol plant waste	Installed at Sorbitol plant	Not required	Yes	Yes
<b>Category 5 - Filtration</b>							
████	Phosphate precipitation + Reverse Osmosis	80% recovery of feed	95%+ reduction	Shelved. Brine disposal issues. High capex	Not required	No	No
████ ████ ████	Low pressure Reverse Osmosis	30% recovery of feed	80% + reduction	Shelved. Brine disposal issues. High capex	Not required	No	No
████ ████	Sand Filter	Not disclosed	20% reduction	Insufficient efficacy	Not required	No	No
<b>Category 6 - Other Approaches</b>							
████ ████	Carbon Aerogels	Not tested	Not tested	Company went out of business. CD also binds other ions	Not tested	No	No
████ ████	Electrochemical	Not disclosed	Higher Nickel due to leaching from electrode plates	Shelved after 4 trials.	Not tested	No	No
████ ████ ████	Ferric Chloride	100ppm	40%	Unscalable due to chloride limits	Not tested	No	No
████ ████	Protein	not tested	Not tested	Lab scale only	Not tested	No	No
████ ████	Hydrogen Peroxide and Ozone	5% w/w + pH adjustment	20% from 150ppb	Significant chemical usage	Not tested	No	No
████ ████	Protein based	Not disclosed	Not tested	Other ions compete with nickel. Not scalable.	Not tested	No	No
████ ████ ████ ████	pH Swing	1-3% w/w	30% from 150ppb	Very high chemical usage.	Not tested	No	No

	pH >11.0	1-2% w/w	Complete for ionic regeneration waste	Being piloted at polyol plant for waste stream	Not tested	Yes	Yes
---	----------	----------	---------------------------------------	--	------------	-----	-----

**Table 2: Technical Challenges on Scale Up for Nickel Remediation Chemistries**

<i>Technology / Provider</i>	<i>with cooperative</i>	<i>not determined</i>	<i>Not commercially available</i>	<i>High Dosages required</i>	<i>Results not scalable beyond bench scale</i>	<i>Low recoveries and brine disposal concerns</i>	<i>Technically Feasible (y/n)</i>	<i>Comments</i>
	X		X				No	
		X		X			No	Would require 5 million pounds of additive per day
			X	X			No	
	X			X			No	
				X			No	Requires a pH to <2 then to pH 5.5 then to pH 10
	X						No	
					X		No	Plant pilot trial did not achieve required Nickel reduction.
		X			X		No	Plant pilot trial did not achieve required Nickel reduction.
					X		No	Plant pilot trial did not achieve required Nickel reduction.
			X				No	

[REDACTED]							No	
[REDACTED]				X			No	
[REDACTED]							No	Decolorization resin needs 3,000 cubic feet of resin at \$300/cubic foot. Resin, beds and regeneration equipment estimated at \$8 - 10 million and uses Ethanol to regenerate resin.
[REDACTED]				X			No	
[REDACTED]		X		X			No	
[REDACTED]							Yes*	Installed at Sorbitol plant
[REDACTED]						X	No	
[REDACTED]							No	
[REDACTED]						X	No	
[REDACTED]						X	No	
[REDACTED]							No	
[REDACTED]			X				No	
[REDACTED]		X	X				No	
[REDACTED]		X					No	Requires over 30,000 pounds of ferric salts per day
[REDACTED]				X			No	
[REDACTED]		X					No	Raise the pH 10 and add ozone and hydrogen

								peroxide. Large amounts of chemicals required.
██████████ █			X				No	
██████████ ██████████ ██████████ ██████████							Yes	Suitable for <~50,000 GPD, non-grain based wastewater with non-chelated, salt-form nickel such as Polyols Plant IX regen waste

\* The amount of used ion exchange resin is limited and it is most effective on non-chelated nickel. Therefore, it is being used to capture nickel from the sorbitol process.

Table 3: Capital and Operating Costs for Nickel Removal at ADM Decatur Complex			
	Initial Capital Cost	Annual Operating & Chemical Costs	Status
<b>Active Projects</b>			
1) Soybean Process Stream Alternative	\$2.7 million	\$400,000	Planned
2) Used IX resin system at Sorbitol Plant	\$450,000	\$200,000	Installed
3) High pH precipitation at Polyols Plant	\$750,000	\$600,000	Planned
<b>Further Technical Analysis/Cost Prohibitive</b>			
1) Polymeric DTC addition and nickel removal using different unit operations			Being piloted
a) <i>Settling Clarifier and Sand Filter</i>	\$25.58 million	\$7.2 million	Being piloted
b) <i>Sand Float Filter</i>	\$23.14 million	\$7.2 million	Being piloted

06/30/2014 - \* \* \* R2014-024 \* \* \*

c) Sand Filter + precipitation	\$24.48 million	\$7.2 million	Being piloted
d) DE Filtration + Precipitation	\$14.97 million	\$7.2 million	Being piloted
e) DE Filtration	\$ 7.05 million	\$7.2 million	Being piloted
f) Sand Filter	\$13.57 million	\$7.2 million	Being piloted

## 2 Reduction in total and soluble nickel between ADM Discharge and SDD effluent

We ran a 5 week trial where in Front and Damon were monitored and compared to corresponding results for SDD Influent and Effluent. While some variability was seen in nickel reduction to SDD influent we are seeing a consistent 80% reduction in total nickel and 59% in soluble nickel to the SDD effluent from the effluent as shown in Table 4.

Table 4: Reduction in total and soluble Nickel between ADM and SDD												
Date	Front	Damon	Flow Averaged F+D	SDD Influent	SDD Effluent	Front	Damon	Flow Average F+D	SDD Influent	SDD Effluent	% Reduction in flow averaged Total Nickel	% Reduction in Flow averaged soluble nickel
	Total				Soluble							
1/9/2012	0.1195	0.1240	0.1217	0.0562	0.0270	0.0521	0.0563	0.0542	0.0299	0.0277	78%	49%
1/11/2012	0.1244	0.1172	0.1132	0.0267	0.0254	0.0563	0.0584	0.0537	0.0250	0.0241	78%	55%
1/13/2012	0.1250	0.0904	0.1321	0.0343	0.0286	0.0498	0.0541	0.0637	0.0266	0.0285	78%	55%
1/16/2012	0.1180	0.0933	0.1281	0.0507	0.0255	0.0516	0.0541	0.0641	0.0264	0.0259	80%	60%
1/18/2012	0.1170	0.1078	0.1286	0.0990	0.0242	0.0530	0.0567	0.0628	0.0237	0.0231	81%	63%
1/20/2012	0.0960	0.0703	0.1138	0.0653	0.0274	0.0368	0.0563	0.0637	0.0271	0.0273	76%	57%
1/23/2012	0.1190	0.0930	0.1242	0.0627	0.0285	0.0533	0.0581	0.0652	0.0268	0.0278	77%	57%
1/27/2012	0.1110	0.1017	0.1200	0.0353	0.0149	0.0421	0.0467	0.0501	0.0108	0.0145	88%	71%
1/30/2012	0.1190	0.1034	0.1248	0.0455	0.0161	0.0542	0.0501	0.0585	0.0171	0.0164	87%	72%
2/1/2012	0.1164	0.1413	0.1298	0.0815	0.0216	0.0491	0.0496	0.0497	0.0240	0.0220	83%	56%
2/3/2012	0.1058	0.1304	0.1197	0.2769	0.0245	0.0500	0.0520	0.0517	0.0404	0.0262	80%	49%
										Average	80%	59%



06/30/2014 - \* \* \* R2014-024 \* \* \*

ADM continues to operate its pilot plant for chemical sequestration of nickel as needed. Since fall 2011, the chemicals being investigated at the pilot plant have been narrowed to those from Nalco and Hydrite.

*“By July 1, 2012 the District must complete the following tasks:*

*Submit a final compliance plan to [the Agency] containing nickel and zinc controls, treatment technologies, proposed permit modifications, or proposed site-specific water quality standards that will achieve compliance with permit limits.*

*- ADM / SDD Variance, p. 29.*

ADM met with the SDD and IEPA on May 8, 2012 and provided them with an overview detailing the progress and ADM's compliance efforts. In addition it was agreed that our petition to the PCB would be part of the compliance plan for ADM to meet our July 1, 2012 deadline.

### **3 Corn Plant used IX system**

As previously disclosed, ADM has been working to install a used ion exchange resin bed system to capture nickel leaching from the sorbitol process catalyst. This system has been running manually for the past 6 weeks. Thus far, about 5 lbs of nickel have been removed from the treated stream and no nickel has been detected in the effluent. This is shown in [Figure 5](#). We are using 105 cu ft of resin and expect a nickel binding capacity of about 3.4 lbs per cubic ft.

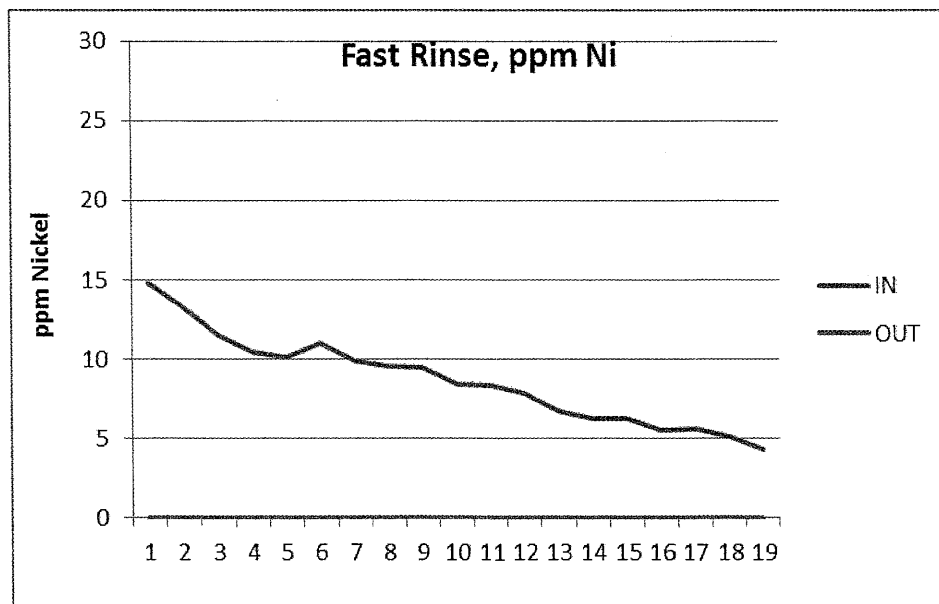


Figure 5: Used ion exchange resin treating material leaving the sorbitol process

In addition we have compiled results for soluble nickel in the refinery waste stream and see a 75% reduction in soluble nickel due to better housekeeping and check filters for capturing waste catalyst.

06/30/2014 - \* \* \* R2014-024 \* \* \*

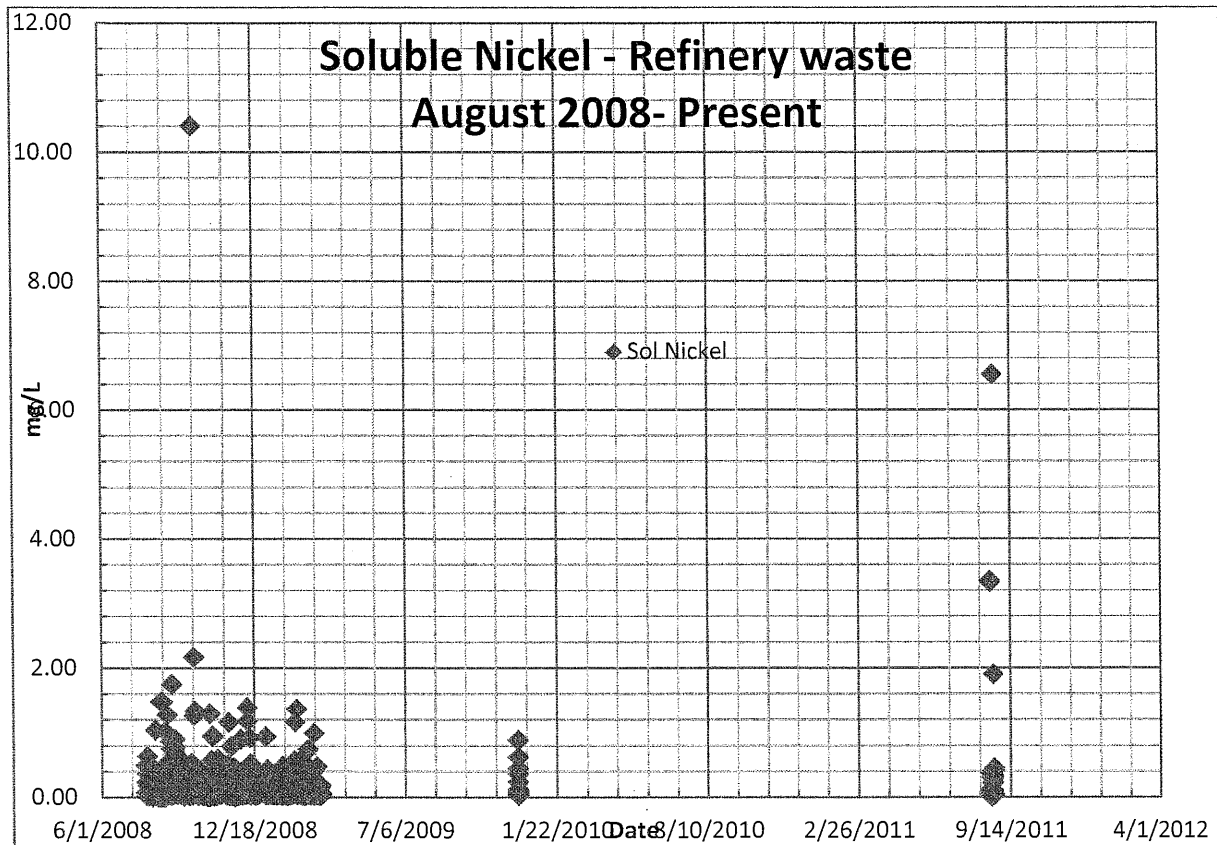


Figure 6 Soluble Nickel reduction on corn plant refinery waste

#### 4 Review Ceased for Technologies

Since the 2011 update, we have ceased trials with polymeric DTC from Kroff 9011 and Hychem DP4. We continue to evaluate the options for scale and will be reporting as progress is made on the same.

#### 5 Polyol waste stream treatment

We have identified our polyol ix waste stream (between 16-22% of total nickel load) as a significant contributor of inorganic nickel due to corrosion of our distillation columns. Initial work using high pH precipitation has shown almost a complete removal of soluble nickel.

Initial work suggests a pH modification would eliminate all soluble nickel from the IX regen streams with chemical costs about \$300 per day.

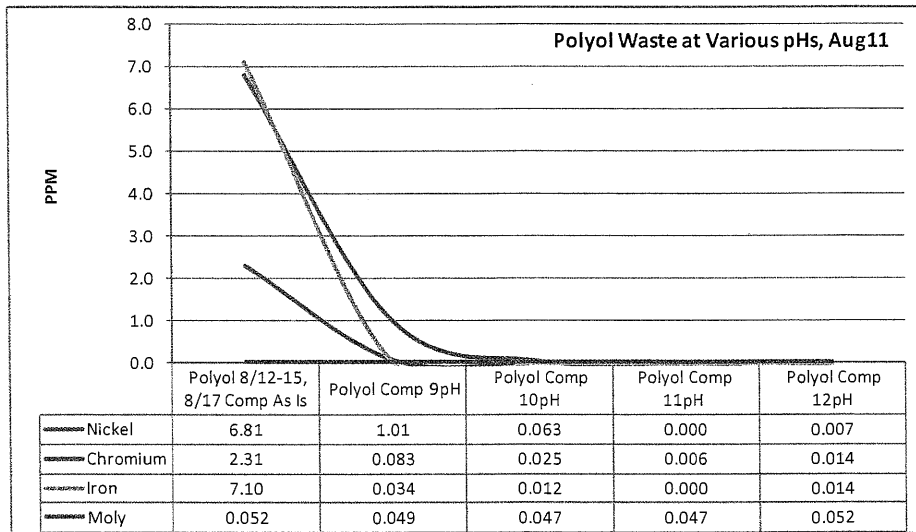


Figure 7 Effect of pH on precipitation on Polyol ion exchange regeneration streams.

				Adjust to 10pH:	
2.5	%NaOH, w/w	Polyol Flows:	lbs / day	lbs 50% NaOH / day	\$ / day
90	sample, ml	8/12/11	61,400	3,014	\$301
10.45	g NaOH to 9pH	8/13/11	65,400	3,210	\$321
10.6	g NaOH to 10pH	8/14/11	60,730	2,981	\$298
10.8	g NaOH to 11pH	8/15/11	119,800	5,880	\$588
16.4	g NaOH to 12.2pH				
\$0.10	50% Caust / lb				
1.6	Starting pH				

The Process Development group at ADM BioProducts has investigated using gypsum (Table 7) as a filter media and seen nickel reductions over using a 0.1um Filter (Table 6).

Sample (ppm)	Ni	Zn	
Waste Water Feed	860.32	3.76	
Waste water/NaOH solution	658.897	2.90	
Treated and filtered waste water	0.300	0.015	

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Note:** Feed was a composite of the discharge from the acid-in and slow rinse cycle in a proportion that is representative of the volume of water used in each cycle. Precipitate was passed through a Buchner filter with a 0.1um filter.

<b>Table 7: Gypsum Filtration of Polyol IX regeneration stream</b>			
Sample Name	Ni	Zn	
	mg/kg	mg/kg	
Waste water/NaOH solution	689.0	2.66	
Treated and filtered waste water	81.94	0.705	

**Note:** Feed was a composite of the discharge from the acid-in and slow rinse cycle in a proportion that is representative of the volume of water used in each cycle. Precipitated feed was fed to a Buchner funnel with CaSO<sub>4</sub> as filter media.

06/30/2014 - \* \* \* R2014-024 \* \* \*

## 6 Appendix A Respirometer and Nitratox Testing

Results from Respirometer and Nitratox testing of Decatur Sanitary Districts MLSS using nickel reduction chemistries piloted at ADM.

Riverbend Laboratories performed respirometer and Nitratox testing of the four chemistries currently being testing using SDD's MLSS. The chemistries were dosed at ~20ppm and ~200ppm and diluted 50:50 with fresh DAF to simulate a scenario envisioned by the Decatur Sanitary District.

Toxicity Test ADM Decatur / ALAR Effluent (2) May 2012

---

### Executive Summary:

The following are the results for the ADM Decatur ALAR Effluent for Anaerobic Toxicity

- **The testing showed no definite toxicity at all. There was no trend towards higher concentrations causing more toxicity. This material appears to be safe to use anaerobically.**

### Method:

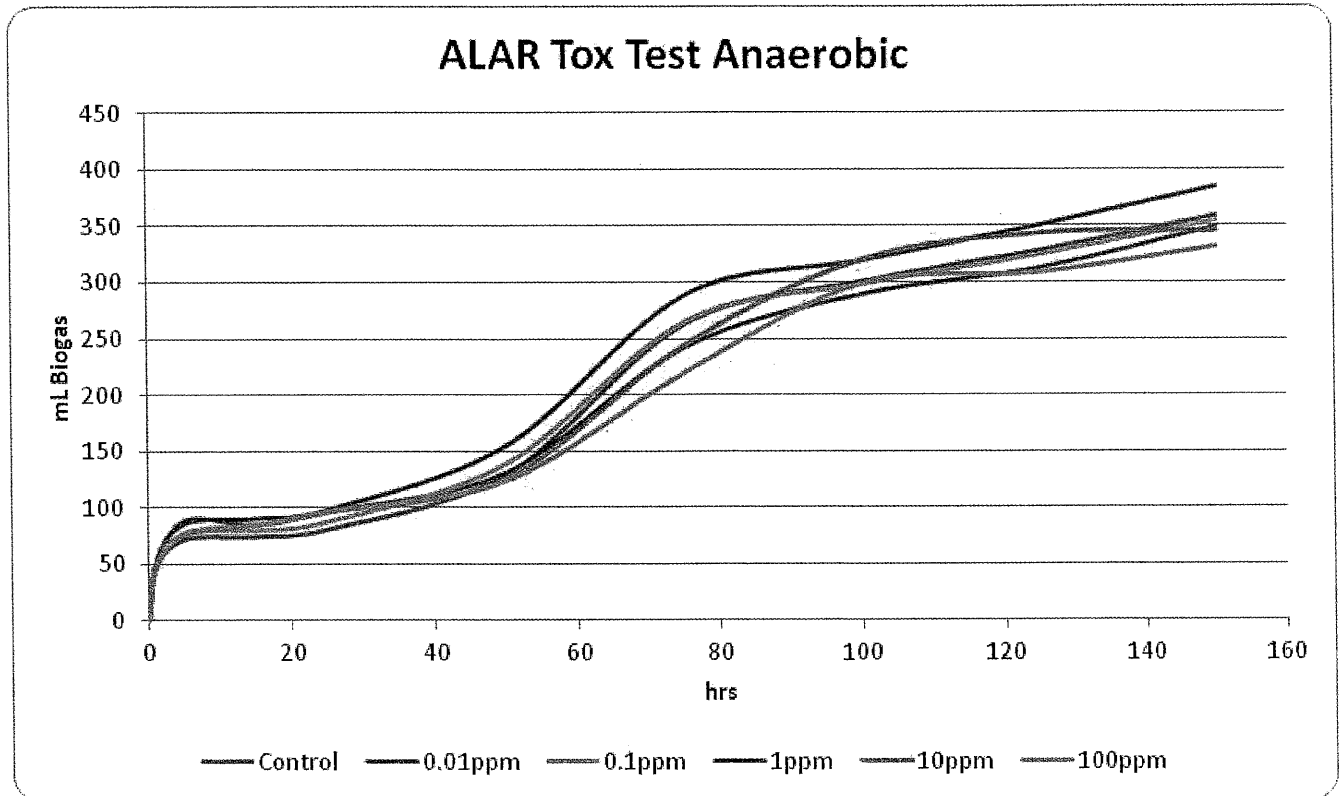
Respirometry measures the biogas generation in mL of the samples. Samples were 200 mL sludge. Each influent was adjusted independently then added to the biomass for each variable the bottles were run at 98deg F and biogas production was recorded. Each bottle had various concentrations of ALAR polymer (raw) added to anaerobic influent and an added concentration of MgOH that was then pH adjusted to 7.5.

- Control – Sludge and normal Influent
- 0.01 ppm – 0.01 ppm ALAR & Sludge and normal Influent
- 0.1 ppm – 0.1 ppm ALAR & Sludge and normal Influent
- 1 ppm – 1 ppm ALAR & Sludge and normal Influent
- 10 ppm - 10 ppm ALAR & Sludge and normal Influent
- 100 ppm - 100 ppm ALAR & Sludge and normal Influent

### Results:

This testing showed that, with equally set up bottles, increasing the concentration of the ALAR chemical had no effect at all. The gas production varied across every concentration, but in general they all followed each other and there was not a statistical difference between the samples, nor a trend as concentrations increased.

06/30/2014 - \* \* \* R2014-024 \* \* \*



ADM & City of Decatur / Respirometry Results (2) / 5/14/12

**Executive Summary:**

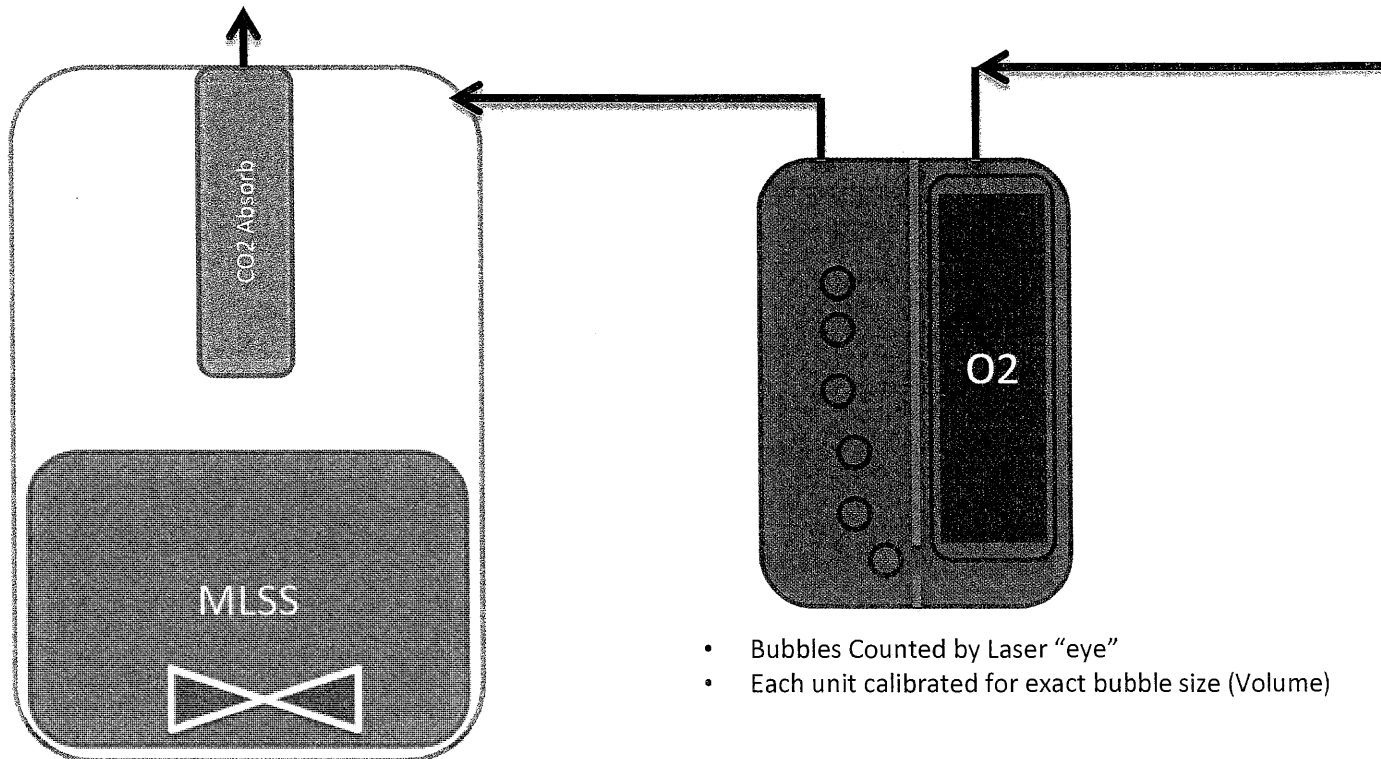
In all cases the chemistries showed no toxicity or inhibition. The lines were almost exactly the same.

I do not think any toxicity exists for this concentration of ALAR effluent.

**Method:**

The method involves setting up several identical bottles on a Challenge Respirometer in aerobic mode. The Challenge Respirometer accurately measures minute changes in oxygen uptake for the bacteria culture in question. This allows us to look at the total possible toxicity to the aeration bacteria (Aerobic Heterotrophs and Nitrifiers combined). By utilizing a control (normal conditions, we can establish a baseline oxygen uptake and then add various amounts of chemicals or suspect waste stream to be tested to see if there are any toxic (lower oxygen uptake) reactions with the biology. In this case all reactors were held at pH 7.5 (+/-0.2) and a temp of 80F (+/- 5.0)

06/30/2014 - \* \* \* R2014-024 \* \* \*



- Bubbles Counted by Laser "eye"
- Each unit calibrated for exact bubble size (Volume)

- Bottle in Bath to hold Temp to Field Conditions
- All Bottles same liquid level
- All Bottles Same rotation Speed

In this test we looked at the following.

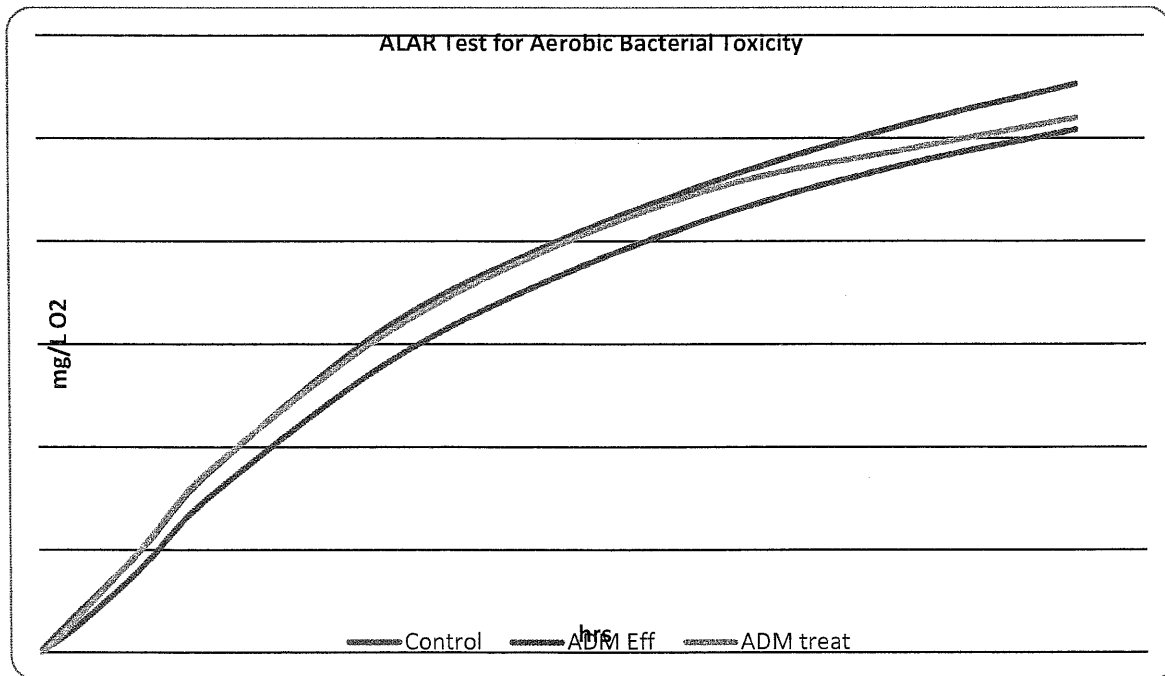
- **Control** – 200 mL Mixed Liquor (city), 100mL City Influent
- **ADM** – 200 mL Mixed Liquor (city), 40mL City Influent, 60mL ADM Effluent
- **ADMALAR** – 200 mL Mixed Liquor (city), 40mL City Influent, 60mL ADM Effluent after ALAR treatment.

#### Results:

Every line matched the control almost exactly, or within statistical error. The slopes also correspond with no negative inflections or deviations. This material seems to not be toxic to Heterotrophic bacteria at the City of Decatur.



06/30/2014 - \* \* \* R2014-024 \* \* \*



#### City Decatur / Nitratox Test Results / 5-10-12

---

#### Executive Summary:

We saw inhibition again in all samples containing City Influent. I included a graph of the last test as well as a good test from last year for comparison below.

#### Method:

The general method involves setting up each test bottle with a specific volume of pure culture nitrifiers, DI water, and a then a specific concentration of NH<sub>4</sub>-N (in this case approx. 100 mg/L). Each bottle is aerated with exactly the same air flow through a diffuser. A control is maintained and then various concentrations of a suspect chemical or waste stream are added to each variable bottle. NH<sub>4</sub>-N is then measured throughout the test (1hr, 8 hrs, 24 hours, 48, hours, 72 hours). All reactors are buffered to 7.5 pH.

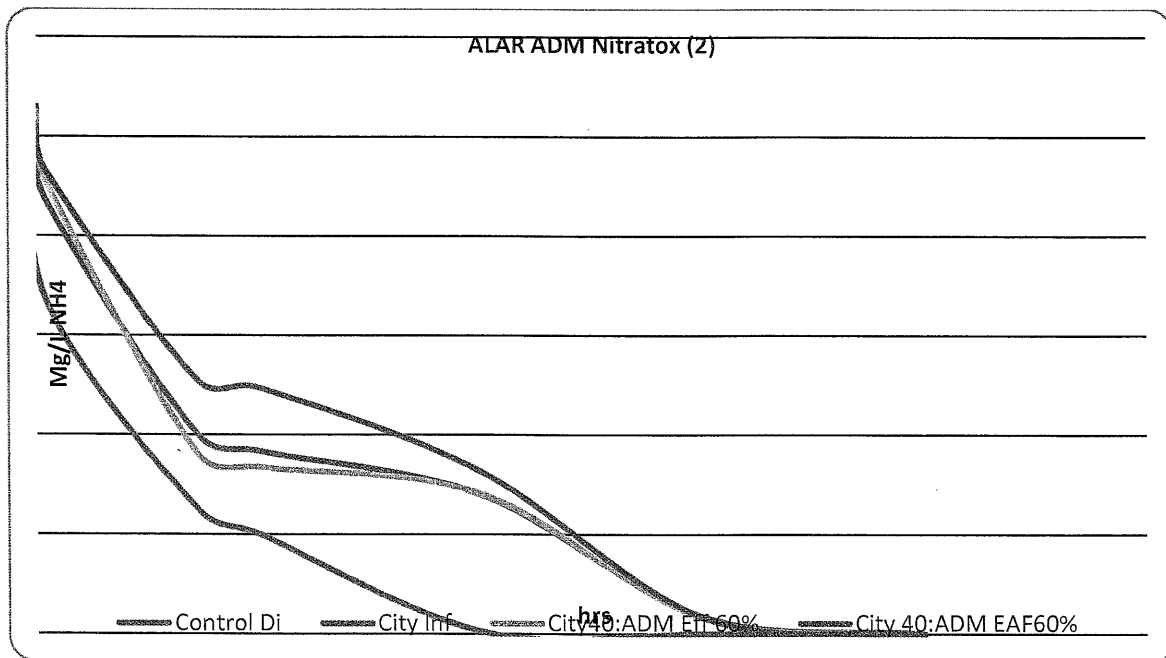
In this test we looked at the following.

- **Control DI** – DI water, Nitrifiers, Ammonia (110 ppm)
- **City Inf** –Nitrifiers, Ammonia (110 ppm) 100% City Influent
- **City40: ADM Eff 60%** – Nitrifiers, Ammonia (110 ppm) 40% City Influent, 60% ADM Effluent.
- **City 40: ADM ALAR60%** - Nitrifiers, Ammonia (110 ppm) 40% City Influent, 60% ADM Effluent after ALAR treatment.

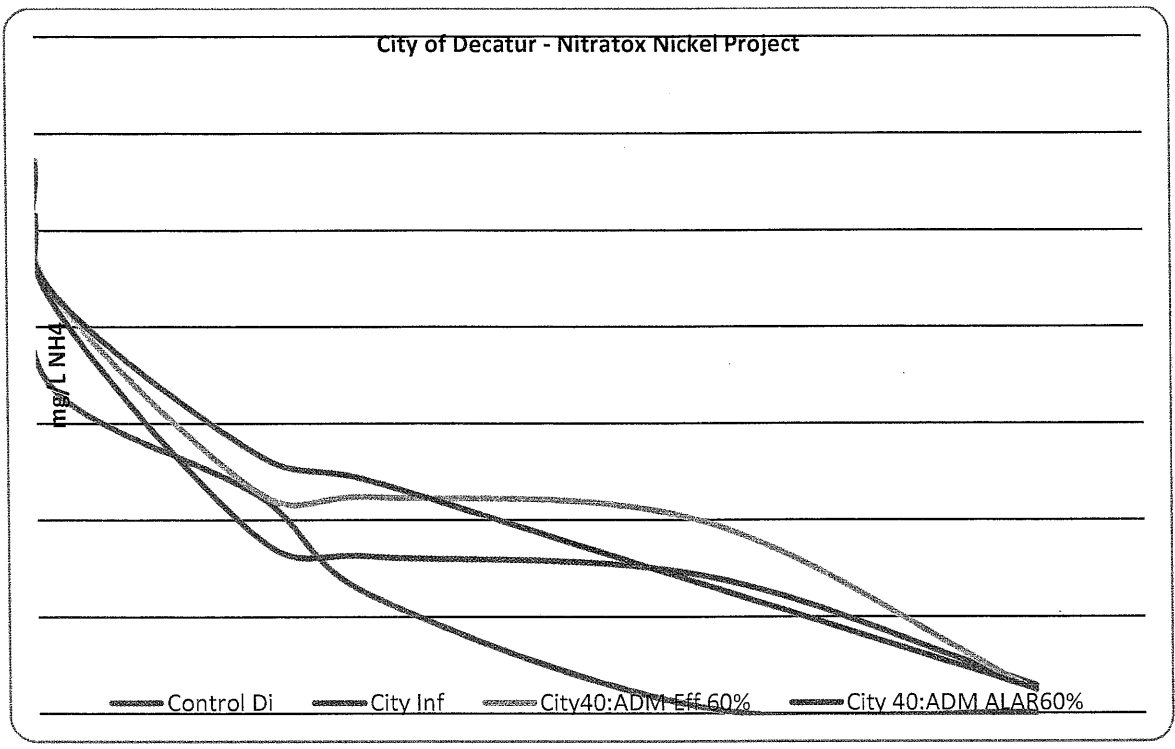
**Results:**

We saw some nitrification inhibition on all samples, but the DI water control. Again this points to something inhibiting on the city influent to nitrification. I have included 2 more graphs besides the normal one for this testing. The second graph is the testing from before.

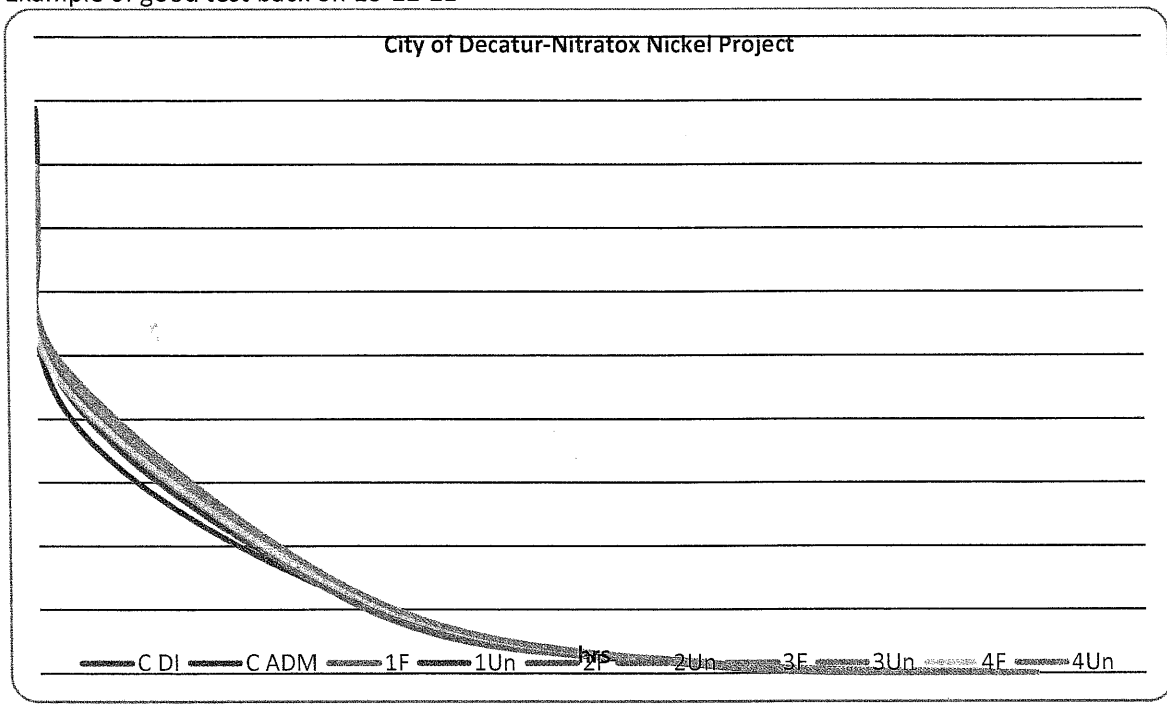
Note the similarity in the curves for the last test and this test. It looks like moderate inhibition to the second step of nitrification, Nitrobacteria. Had the DI water sample responded the same I would have thought it a bad batch of our nitrifiers, but they handled the NH4 fine.



Last Test from last month below



Example of good test back on 10-11-11



## Sanitary District of Decatur

501 DIPPER LANE • DECATUR, ILLINOIS 62522 • 217/422-6931 • FAX: 217/423-8171

December 19, 2012

Illinois Environmental Protection Agency  
Bureau of Water Compliance Assurance Section, MC #19  
1021 North Grand Avenue East  
P.O. Box 19276  
Springfield, Illinois 62794-9276

Re: NPDES Permit IL0028321  
IPCB Order PCB 09-125  
Interim Report

Dear Sir or Madam:

Enclosed is the Interim Report regarding compliance with nickel and zinc limits required by Special Condition 18 of the Sanitary District of Decatur's NPDES Permit and the Pollution Control Board Order in PCB 09-125.

Please contact me at 422-6931 ext. 214 or at [timk@sdd.dst.il.us](mailto:timk@sdd.dst.il.us) if you have any questions regarding this report.

Sincerely,



Timothy R. Kluge, P.E.  
Technical Director

cc: Rick Pinneo, IEPA (via email)  
Bob Mosher, IEPA (via email)  
SDD File

06/30/2014 - \* \* \* R2014-024 \* \* \*

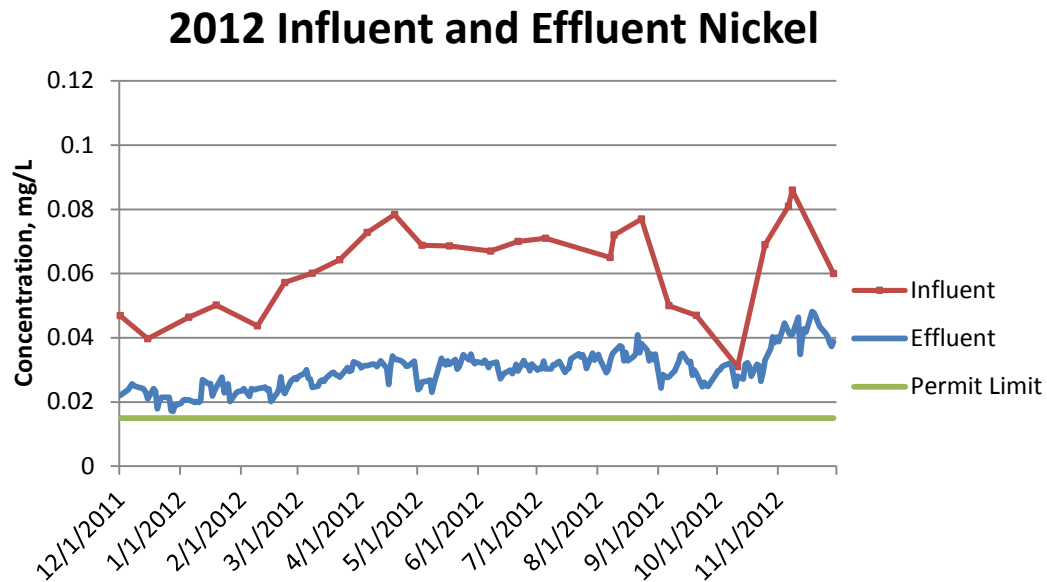
**Sanitary District of Decatur  
Nickel and Zinc Limits  
December 2012 Interim Report**

The modified NPDES permit for the Sanitary District of Decatur that became effective July 1, 2009 contains limits for nickel and zinc and a one-year compliance schedule extension for meeting the limits. Special Condition 17 requires the District to achieve compliance with final nickel and zinc effluent limitations by July 1, 2010. This Special Condition also notes that the permit may be modified to include revised compliance dates in Pollution Control Board orders, and that prior to such permit modification, the revised dates in the appropriate orders shall govern the Permittee's compliance.

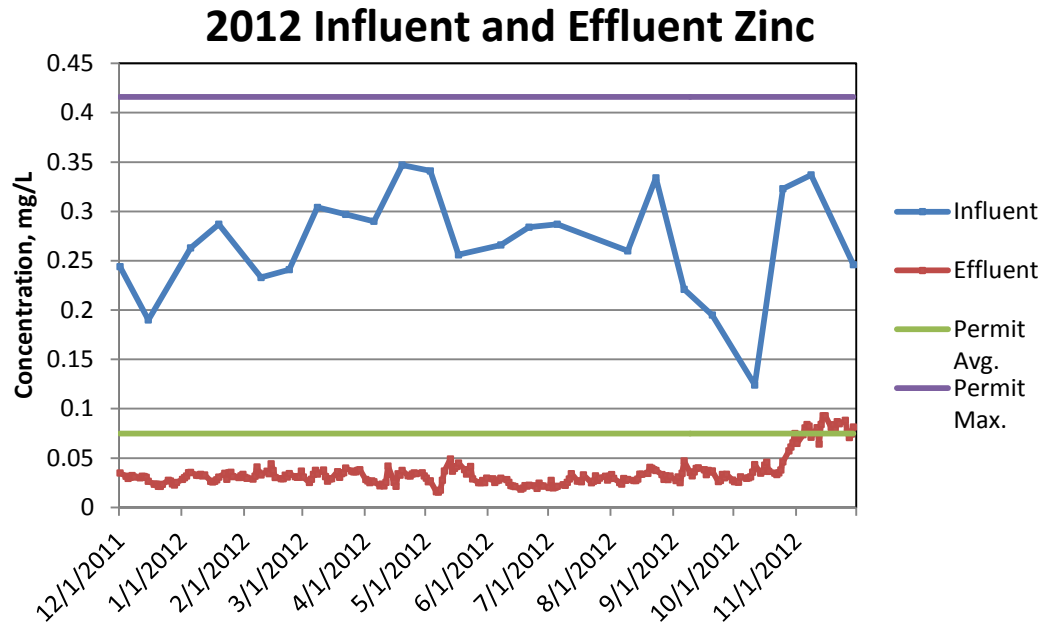
On January 7, 2010 the Illinois Pollution Control Board granted a variance to the District allowing additional time to comply with final permit limits (PCB 09-125). The final compliance date contained in the Board Order is July 1, 2014. The District's NPDES Permit has not yet been modified or reissued to incorporate the variance. The Board Order also requires that an interim report be submitted to Illinois EPA by January 1, 2013. This report is submitted to meet both the permit and variance requirements.

**Plant Influent and Effluent Sampling**

Ongoing influent sampling for nickel and zinc continues at a frequency of twice monthly, and effluent sampling is done five days per week according to NPDES monitoring requirements. A summary of influent and effluent values during the past twelve months is shown below.



06/30/2014 - \* \* \* R2014-024 \* \* \*



Data shows that the plant effluent is not able to consistently meet the current nickel permit limit. Effluent zinc concentrations remain at or below the permit limit.

### Receiving Stream Sampling

Upstream and downstream sampling continues at a twice monthly frequency to provide a more complete picture of nickel and zinc in the Sangamon River. One upstream and four downstream sampling sites are being monitored. A summary of 2011-2012 river monitoring data is attached. Downstream nickel results remain high during times of low upstream river flow; low flows have prevailed during most of the past two years. With one exception, upstream and downstream zinc results during 2011 and 2012 have been below the Illinois water quality standard.

### Pretreatment Ordinance Limits

The District's pretreatment ordinance was amended in October 2009 as noted in previous interim reports.

### Stream Flow-Based Compliance Options

The District continues investigation of flow-based permit limits, to take advantage of upstream flow for mixing when it is available. A USGS flow gauging station is located about two miles upstream of the District's discharge point, and provides near-real time flow information. A proposal for flow-based limits will be a part of relief requested from the Pollution Control Board.

06/30/2014 - \* \* \* R2014-024 \* \* \*

### **Water Quality Standard Investigations**

The District is in the final stages of preparing a petition for a site-specific nickel standard, which we expect to file with the Pollution Control Board in the very near future. Comments and questions received from U.S. EPA on December 7, 2012 are being evaluated.

We are also following the Pollution Control Board rulemaking currently underway to correct an error found in the existing zinc water quality standard. If the Board adopts the corrected standard, utilizing the corrected number to determine our permit limit should provide further assurance of compliance.

### **Industrial Source Sampling and Investigations**

Sampling at Archer Daniels Midland Company for metals continues at a frequency of twice monthly and other industries discharging metals are sampled quarterly. Sample results obtained from ADM within the past two years are attached.

The District's operating permit issued to ADM was modified on November 18, 2009 and again on June 17, 2010 to reflect the new limits and provide a compliance schedule for meeting the limits. Final local limits will be determined following Board action on the District's site-specific WQS request.

Both ADM and Tate & Lyle formerly utilized zinc as part of their cooling tower treatment programs, and both have eliminated or greatly reduced zinc in their towers. At this time, both industries are meeting the zinc pretreatment limit. ADM is continuing to investigate the possible impact of the zinc limit on their planned wasting of solids from their pretreatment system to the District's collection system.

The discharge from ADM is by far the most significant industrial source of nickel. ADM has been very active in seeking treatment technology for nickel removal, involving plant management and research department personnel in addition to environmental compliance and legal staff. District staff met with ADM personnel several times during the past year, most recently on November 30, 2012. The District's pretreatment permit requires semi-annual reports of ADM's investigations, and the most recent report is attached. Completed and anticipated modifications made by ADM are listed on page 4 of the report.

### **Additional Pretreatment Limit Investigations**

Pretreatment ordinance limits adopted in 2009 were adopted as total (rather than soluble) limits based on review of soluble/insoluble data. Refinement of pretreatment limits is an ongoing process and will depend on final permit limits as well as treatment technologies that might be employed by industrial users.

## **Compliance Plan**

In summary, the District's compliance plan includes the following:

1. Continue to work with ADM to implement nickel discharge reductions and removal technologies. ADM's November 30, 2012 Interim Report describes the completed and planned reductions.
2. Complete and file a petition for a site-specific water quality standard for nickel, based on bioavailability. We have been working with Illinois EPA to address questions and comments through the summer and fall of 2012. Currently we are evaluating comments and questions received from U.S. EPA on December 7, 2012.
3. The Board petition will contain a request for variable permit limits based on the amount of flow available in the Sangamon River.





06/30/2014 - \* \* \* R2014-024 \* \* \*

ADM Nickel and Zinc Results				
	ADM Point A	ADM Point A	ADM Point D	ADM Point D
Sample	Nickel, Tot	Zinc, Tot	Nickel, Tot	Zinc, Tot
Date	mg/L	mg/L	mg/L	mg/L
1/5/2011	0.0629	0.53	0.0669	0.204
1/10/2011	0.0577	0.495	0.0666	0.188
2/7/2011	0.0836	0.756	0.0892	0.329
2/14/2011	0.0589	0.472	0.0598	0.18
3/7/2011	0.0773	0.447	0.0627	0.128
3/14/2011	0.086	0.51	0.1	0.449
4/4/2011	0.07	0.428	0.0841	0.387
4/20/2011	0.0687	0.33	0.0861	0.347
5/2/2011	0.0712	0.304	0.0809	0.302
5/9/2011	0.06	0.301	0.0712	0.3
6/6/2011	0.0648	0.285	0.0786	0.276
6/13/2011	0.0692	0.293	0.0809	0.314
7/11/2011	0.0542	0.226	0.0625	0.209
8/1/2011	0.0491	0.165	0.0621	0.172
8/8/2011	0.0567	0.215	0.074	0.242
9/1/2011	0.0662	0.285	0.0842	0.327
9/7/2011	0.0684	0.311	0.0884	0.344
10/3/2011	0.094	0.518	0.114	0.515
10/10/2011	0.0643	0.191	0.073	0.189
11/7/2011	0.0912	0.377	0.116	0.529
11/22/2011	0.221	1.28	0.136	0.623
12/1/2011	0.0917	0.416	0.11	0.492
12/5/2011	0.094	0.423	0.117	0.508
1/5/2012	0.0921	0.451	0.111	0.531
1/9/2012	0.0868	0.424	0.109	0.491
2/6/2012	0.121	0.441	0.134	0.488
2/13/2012	0.127	0.49	0.159	0.601
3/5/2012	0.128	0.431	0.15	0.493
3/12/2012	0.12	0.406	0.141	0.482
4/12/2012	0.169	0.621	0.191	0.705
4/19/2012	0.148	0.516	0.176	0.674
5/1/2012	0.0797	0.251	0.152	0.564
5/7/2012	0.137	0.494	0.141	0.448
6/4/2012	0.133	0.412	0.147	0.468
6/11/2012	0.12	0.366	0.144	0.452
7/2/2012	0.129	0.375	0.158	0.462
7/9/2012	0.109	0.322	0.132	0.402
8/1/2012	0.127	0.426	0.17	0.574
8/6/2012	0.097	0.193	0.12	0.242
9/6/2012	0.105	0.289	0.117	0.271
9/10/2012	0.479	0.531	0.165	0.559
10/1/2012	0.15	0.46	0.168	0.54
10/8/2012	0.129	0.421	0.152	0.444
11/1/2012	0.16	0.487	0.184	0.568
11/12/2012	0.158	0.444	0.197	0.525

06/30/2014 - \* \* \* R2014-024 \* \* \*

To: Illinois Environmental Protection Agency  
Decatur Sanitary District

From: ADM Decatur WWTP

CC: ADM Corn Processing, ADM Oilseeds Processing, ADM JRRRC

Date: November 30, 2012

Re: Status Report Compliance Strategy for 2012 for Decatur Sanitary District and ADM  
Decatur WWTP for waste treatment. (Covers updates post June 2012- date)



**Table of Contents**

\_Toc341675751

1	Background and Update (post June 2012) .....	3
2	ADM Pilot trials update .....	16
2.1	Precipitation of Nickel .....	16
2.2	Membrane Filtration .....	32
2.3	Proprietary adsorbent .....	33
2.4	Other approaches .....	34
2.5	Toxicity trials .....	35
3	Corn Plant used IX system .....	36
4	Review Ceased for Technologies .....	37
5	Polyols IX waste stream treatment .....	37
6	Respirometer and Nitratox Testing .....	38

06/30/2014 - \* \* \* R2014-024 \* \* \*

ADM Research and Decatur complex have been actively pursuing technologies to remove Nickel (Ni) from its effluent stream released to the SDD treatment plant. As part of our Industrial Users permit we are enclosing our updated technical report on our efforts to mitigate nickel in the Decatur complex effluent.

*The IU shall submit reports to the SDD by December 1, 2011, and June 1 and December 1, 2012 detailing their progress concerning reducing their effluent concentrations of nickel and zinc from current levels to levels that will not exceed those shown in Section E, paragraph 7, of this permit*

*- ADM SDD Industrial Users Permit 200.*

ADM met with the SDD and IEPA in June 2012 and provided them with an overview detailing the progress and ADM's compliance efforts. In addition ADM has provided the district and its attorneys with input in finalizing a draft petition for site specific rulemaking being discussed with IEPA. Enclosed is a report on the progress ADM has made since the last update issued on June 2012.

#### **1 Background and Update (post June 2012)**

Nickel and Zinc are present in effluent leaving the ADM Decatur Complex Waste Water plant. Of the two metals, nickel is more difficult to remove from the effluent. ADM has conducted 5 plant material balances to understand the sources of Nickel in its internal streams. ADM's Decatur Complex consists of multiple, separate processing plants, which send wastewater to the on-site wastewater treatment plant ("WWTP") operated by Corn Plant personnel. These processing plants consist of the Corn Wet Mill, BioProducts Plant, Cogeneration Plant, East Soybean Processing Plant, West Soybean Processing Plant, Vitamin E Plant, Corn Germ Processing Plant, Glycols Plant and the Polyols Plant. Each of these unique plants produces multiple products, using both batch and continuous processes, and creates water streams which generally are reused multiple times prior to being discharged to the WWTP. The WWTP treats approximately 11 MGD through a newer anaerobic treatment system followed by aerobic treatment prior to discharge to the District.

The incoming soybeans contain approximately 4.1 parts per million ("ppm") nickels, while incoming corn contains approximately 0.53 ppm nickel. Given that ADM's Decatur Complex processes approximately 600,000 bushels of corn and 200,000 bushels of soybeans per day, our incoming Nickel load is about 49.2 lbs from the soybeans and 19.1 lbs from the corn. A small portion of the incoming nickel is discharged in the effluent.

06/30/2014 - \* \* \* R2014-024 \* \* \*

In the ADM Decatur Facility, effluent water originates in the corn and soybeans being processed at the facility. During the processing, the metals are released and enter the processing water, some of which eventually ends up at the wastewater treatment plant.

ADM has monitored soluble Nickel at the Damon and Front stations continuously (see [Figures 1-3](#)) and made a number of modifications in its operations:

- 1) Our nickel in effluent discharge has been fairly stable and trending slightly down.
- 2) Spent catalyst from the West Soybean Processing Plant is collected and sent to a landfill. Spilled catalyst is collected and disposed of as solid rather than washed into a sump.
- 3) Particulate catalyst from the Corn Plant Sorbitol production is captured by filters and physically recovered for recycling or disposal. ADM has installed an ion exchange resin system at the Sorbitol Plant to capture soluble nickel from wastewater. The system is undergoing startup and troubleshooting and results from testing are reported later in the current report.
- 4) The East Soybean Processing Plant is finalizing its design of a system that will remove the soy molasses stream (containing approximately 2.4 lb/day, approximately 35% of the soluble nickel from the Decatur Complex) from going to the WWTP. This stream is high in digestible, fermentable sugars but will need to be concentrated for stability. The East Soybean Processing Plant has prepared a cost estimate for this process change. Once the system design is complete and the cost estimate approved, ADM anticipates spending several million dollars to install it. Our anticipated start date for this project is late 2013 pending environmental and regulatory approvals.
- 5) The Polyols Plant accounts for approximately 11% of the soluble nickel from the Decatur Complex. The Polyols Plant has determined this nickel can be precipitated by pH adjustment. ADM is now determining how to implement this change on its process stream. As described later in this report, an internal request for funding ("AFE") has been submitted and we expect startup in later 2013 pending environmental and regulatory approvals.
- 6) We have also collected soluble nickel data for the past 8+ yrs. and it shows that our soluble nickel number remains largely unchanged with the only exception being the

change in total nickel due to startup of the anaerobic digesters post August 2008 (this data was shared in June 2012 update).

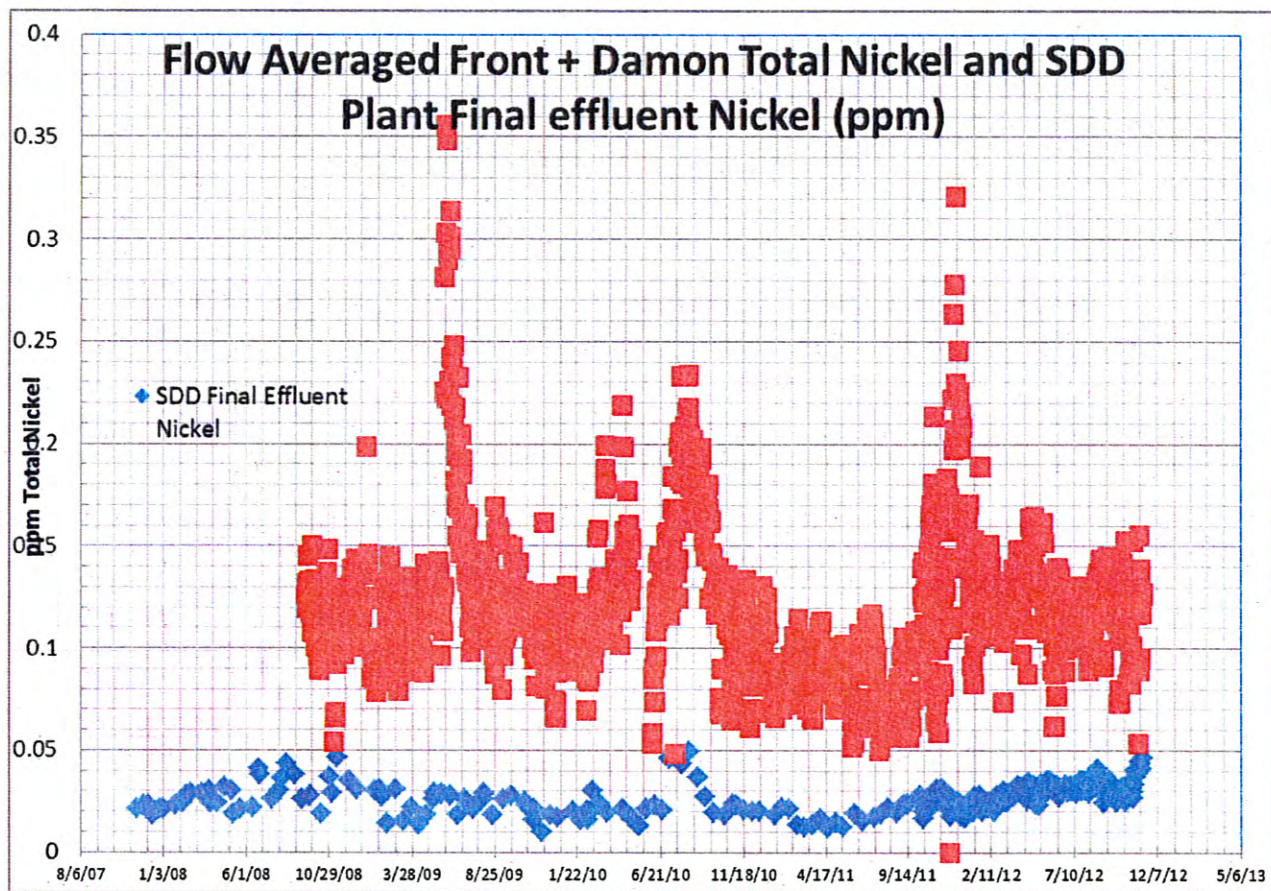


Figure 1 Flow Averaged Front and Damon Nickel

06/30/2014 - \* \* \* R2014-024 \* \* \*

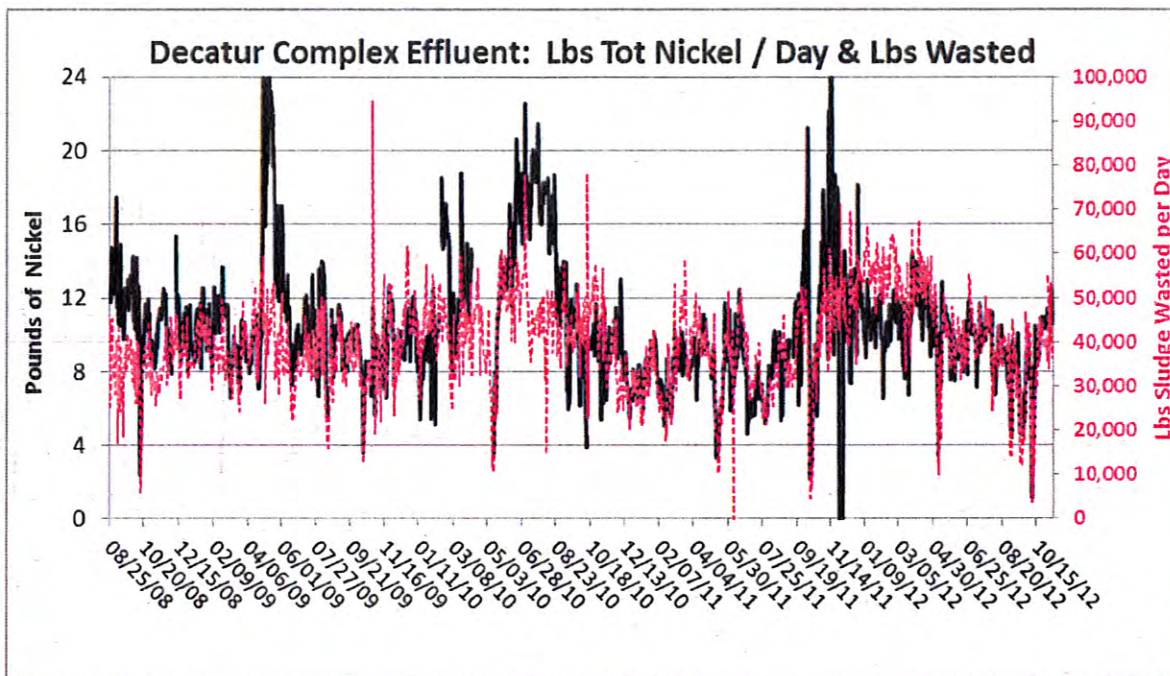


Figure 2 Decatur complex effluent- sludge wasting and nickel in effluent

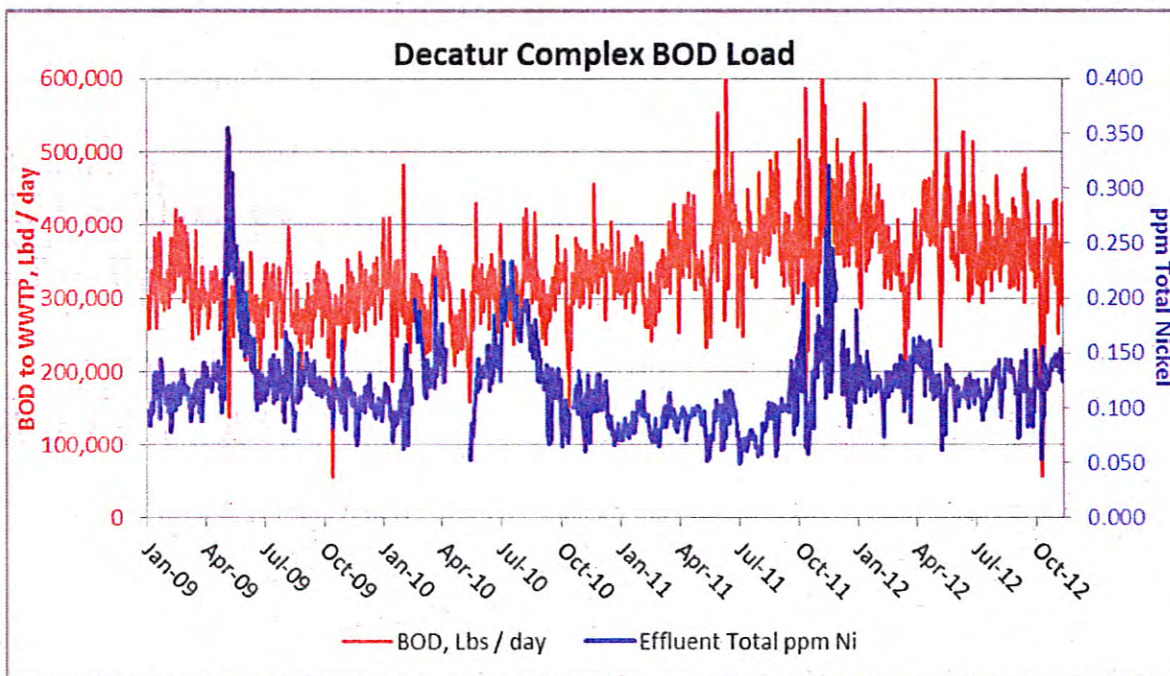


Figure 3 Decatur complex effluent- BOD and nickel in effluent



06/30/2014 - \* \* \* R2014-024 \* \* \*

As reported in the 2010 (summer) - 2012 (summer) updates, ADM has, thus far, investigated 46 technologies that had the potential to control nickel at the Decatur Complex WWTP. (This was in addition to the work ADM has undertaken to reduce nickel within the individual wastewater streams.)

As indicated in Table 1, these technologies can be segregated into six broad categories:

1. Nickel Proprietary Precipitation Process;
2. Nickel Chemical Precipitation;
3. Ion Exchange Resin;
4. Filtration;
5. pH Modification
6. Noncommercial, Experimental Technologies.

Additional details about some of the technologies identified in Table 1 are presented in Table 2, including a general list of reasons why certain of those technologies are not technically feasible and are not currently being pursued.

ADM has finished piloting the various technologies listed in our summer 2012 report. Table 3, summarizes the capital, operating and chemical costs for the approaches it is scaling and either installing or continuing to trial and a summary of their best results.

Thus, of all of the technologies investigated by ADM to date, the only viable option that has not already been fully planned, installed or employed by ADM is the nickel capture process based upon high pH precipitation at the Polyols Plant. Because such technology has been determined to be both technically feasible and economically reasonable for the specific application, ADM will install that system at the Polyols Plant after necessary pilot testing is complete. However, that reduction, even when combined with the other reductions achieved by ADM, will still not reduce nickel to the levels sought by the District under its current permit. Even if ADM could overcome the technical obstacles it faces regarding the use of polymeric dimethyl dithiocarbamate to reduce nickel from the final wastewater effluent, testing indicates that residual soluble nickel concentrations close to 0.050 mg/L will remain irrespective of contact time and incoming nickel levels. ADM's investment from 2009 to December 2011 to identify and implement viable solutions to meet the nickel standard has been approximately \$1.02 million in employee costs and \$0.45 million in equipment rental and pilot trial costs. In addition, ADM has spent \$0.45 million to install a resin capture system at the Decatur Sorbitol plant. It is also preparing to spend an additional \$2.5 million to install a system to allow removal of the soy molasses stream and roughly \$0.75 million to install a high pH precipitation and filtration process at

the Polyols Plant. ADM has also significantly improved housekeeping in the West Plant to minimize nickel catalyst from entering the wastewater system. Finally, ADM has finished pilot trials on its ability to scale up a potentially viable chemical technology for installation at the Decatur Complex WWTP based on polymeric dimethyl dithiocarbamate to reduce nickel from its effluent. At this point, all reasonably identifiable options have been explored and all technically feasible and economically reasonable solutions are being pursued.

Table 1 Summary of Technologies Reviewed by ADM							
	Chemistry	Dosage	Nickel Reduction (%)	Current Status	Nitrate/Respirometer Testing*	Technically	Economically
<b>Category 1 - Nickel Proprietary Precipitation Process</b>							
	Activated Clay	1%-3% by weight of clay	40%-60% (from 200ppb influent)	Not Active, High dosages unscalable.	Not tested	No	No
	Acidic Clay	4%-8% w/w	40% (from 90ppb influent)	Stopped. High dosage.	Not tested	No	No
	Chitosan Based	5% w/w	90% from 200 ppb influent	Abandoned. High dosage, Concerns with Chitosan Availability	Not tested	No	No

06/30/2014 - \* \* \* R2014-024 \* \* \*

██████████ ██████████ ██████████ ██████████	Proprietary	2% w/w	82% (from 100ppb)	Abandoned. Company went out of business	Not tested	No	No
██████████ ██████████	Proprietary	200 ppm	64% (from 120ppb)	Shelved. Strong pH swing (acidification to pH 2, alkalination to 10 and neutralization)	Not tested	No	No
██████████	Not disclosed	Not disclos ed	40-60% (from 200ppb)	Shelved. Company not sharing samples.	Not tested	No	No
<b>Category 2 - Nickel Chemical Precipitation Process Using Carbamates or Organic Sulfides</b>							
██████████ ██████████ ██████████	Polymeric Dimethyl Dithiocarba mate	100pp m with 50ppm of CaCl2	30% from 150ppb	Piloted. Total Nickel reduction to 60ppb.	Passe d	No	No
██████████	Polymeric Dimethyl Dithiocarba mate	20- 50ppm	60% from 150ppb	Piloted. Total Nickel reduction to 54 ppb.	Passe d	Ye s	No
██████████	Polymeric Dimethyl Dithiocarba mate	100pp m	41% from 150ppb	Piloted. Total Nickel reduction to 32ppb	Passe d	Ye s	No
██████████ ██████████	Dimethyl Dithiocarba mate	50ppm + pH 6.0	76% from 150ppb	Piloted. Nickel reduction seen to 40ppb	Passe d	Ye s	No
██████████ ██████████	Polymeric Dimethyl	300pp m + pH	30%	Not active. Modified chemistry from Nalco	Not tested	No	No

06/30/2014 - \* \* \* R2014-024 \* \* \*

█	Dithiocarbamate	swing		being tested	.		
█	Polymeric Dimethyl Dithiocarbamate	50ppm	48% from 100ppb	Piloted. Nickel reduction seen to 20ppb	Passed	Yes	No
█	Polymeric Dimethyl Dithiocarbamate	200ppm	52% from 150ppb	Piloted. Nickel reduction seen to 39 ppb	Passed	No	No
█	Polymeric Dimethyl Dithiocarbamate	100ppm	40% from 150ppb	Not piloted. GE has not scaled up commercial manufacturing.	Not tested	No	No
█	Dimethyl Dithiocarbamate	100ppm	60% from 150ppb	Piloted. Nickel reduction seen to 24 ppb	Passed	No	No
<b>Category 3 - Non Functional Resins</b>							
█	Styrene Divinyl Benzene	2-5% w/w	20%	Not scaled. High regeneration costs	Not tested	No	No
█	Styrene Divinyl Benzene	4% w/w	60%	Not scaled. Very high resin use. Caustic /ethanol based regeneration	Not tested	No	No
█	Immobilized Ion Exchange Beads	5%	Not significant	Shelved	Not tested	No	No
<b>Category 4 - Reuse of Ion Exchange Resin</b>							
█	Sulfonic	0.1-	Complete removal	Installed at Sorbitol	Not	Yes	Yes

06/30/2014 - \* \* \* R2014-024 \* \* \*

██████████ ██████████		0.5%	of Ionic Nickel from the Sorbitol plant waste	plant	requir ed	s	
<b>Category 5 - Filtration</b>							
██████████ ██████████	Phosphate precipitation + Reverse Osmosis	80% recover y of feed	95%+ reduction	Shelved. Brine disposal issues. High capex	Not requir ed	No	No
██████████ ██████████ ██████████ ██████████	Low pressure Reverse Osmosis	30% recover y of feed	80% + reduction	Shelved. Brine disposal issues. High capex	Not requir ed	No	No
██████████ ██████████ ██████████ ██████████	Sand Filter	Not disclos ed	20% reduction	Insufficient efficacy	Not requir ed	No	No
<b>Category 6 - Other Approaches</b>							
██████████ ██████████ ██████████	Carbon Aerogels	Not tested	Not tested	Company went out of business. CD also binds other ions	Not tested	No	No
██████████ ██████████ ██████████	Electrochem ical	Not disclos ed	Higher Nickel due to leaching from electrode plates	Shelved after 4 trials.	Not tested	No	No
██████████ ██████████ ██████████	Ferric Chloride	100pp m	40%	Unscalable due to chloride limits	Not tested	No	No
██████████ ██████████	Protein	not tested	Not tested	Lab scale only	Not tested	No	No

06/30/2014 - \* \* \* R2014-024 \* \* \*

██████████	Hydrogen Peroxide and Ozone	5% w/w + pH adjustment	20% from 150ppb	Significant chemical usage	Not tested	No	No
██████████	Protein based	Not disclosed	Not tested	Other ions compete with nickel. Not scalable.	Not tested	No	No
██████████	pH Swing	1-3% w/w	30% from 150ppb	Very high chemical usage.	Not tested	No	No
██████████	pH >11.0	1-2% w/w	Complete for ionic regeneration waste	Being piloted at Polyols plant for waste stream	Not tested	Yes	Yes
██████████	Proprietary Adsorbent	5%	Reduced soluble nickel to below 0.037ppb	Bench scale trials complete. Unable to scale up due to startup nature of technology	Not tested	No	No

**Table 2: Technical Challenges on Scale Up for Nickel Remediation Chemistries**

Technology / Provider	Vendor not cooperative with samples	Assessed and determined not effective	Not commercially available	High Dosages required	Results not scalable beyond bench scale	Low recoveries and brine disposal concerns	Technically Feasible (Y/n)	Comments
██████████	X		X				No	
██████████		X		X			No	Would require 5 million pounds of additive per day

06/30/2014 - \* \* \* R2014-024 \* \* \*

[REDACTED]			X	X			No	
[REDACTED]	X			X			No	
[REDACTED]				X			No	Requires a pH to <2 then to pH 5.5 then to pH 10
[REDACTED]	X						No	
[REDACTED]					X		No	Plant pilot trial did not achieve required Nickel reduction.
[REDACTED]		X			X		No	Plant pilot trial did not achieve required Nickel reduction.
[REDACTED]					X		No	Plant pilot trial did not achieve required Nickel reduction.
[REDACTED]			X				No	
[REDACTED]							No	
[REDACTED]				X			No	
[REDACTED]				X			No	Decolorization resin needs 3,000 cubic feet of resin at \$300/cubic foot. Resin, beds and regeneration equipment estimated at \$8 - 10 million and uses Ethanol to regenerate resin.
[REDACTED]		X		X			No	
[REDACTED]							Yes	
[REDACTED]							*	Installed at Sorbitol plant
[REDACTED]						X	No	
[REDACTED]						X	No	
[REDACTED]						X	No	

06/30/2014 - \* \* \* R2014-024 \* \* \*

[REDACTED]			X				No	
[REDACTED]		X	X				No	
[REDACTED]		X					No	Requires over 30,000 pounds of ferric salts per day
[REDACTED]			X				No	
[REDACTED]		X					No	Raise the pH 10 and add ozone and hydrogen peroxide. Large amounts of chemicals required.
[REDACTED]			X				No	
[REDACTED]							Yes	Suitable for <~50,000 GPD, non-grain based wastewater with non-chelated, salt-form nickel such as Polyols Plant IX regen waste
[REDACTED]	x		x		x			We are discussing a pilot trial with the vendor but they don't have capabilities to manufacture quantities required.
<p>* The amount of used ion exchange resin is limited and it is most effective on non-chelated nickel. Therefore, it is being used to capture nickel from the sorbitol process.</p>								

	Initial Capital Cost	Annual Operating & Chemical Costs	Status
<b>Active Projects</b>			
1) Soybean Process Stream Alternative	\$2.7 million	\$400,000	Planned
2) Used IX resin system at Sorbitol Plant	\$450,000	\$200,000	Installed



06/30/2014 - \* \* \* R2014-024 \* \* \*

3) High pH precipitation at Polyols Plant	\$750,000	\$600,000	Planned
<b>Further Technical Analysis/Cost Prohibitive</b>			
1) Polymeric DTC addition and nickel removal using different unit operations	Not available	Not available	Pilot trials finished.
a) [REDACTED] Single-Pass Membrane Filter	\$ 25million	\$ 3 million	Effluent Irreversibly fouled Membrane. Filtrate rate decreased more than 90%
b) [REDACTED] Dissolved Air Floatation and Sand Filter	\$ 15 million	\$ 2.3 million	Average nickel reduction insufficient to meet proposed limits
c) [REDACTED] : Dissolved Air Floatation Filter	\$ 25million	\$ 2 million	Average nickel reduction is insufficient to meet proposed limits
d) [REDACTED] : Rotary Vacuum Filter	\$ 1.8 million	\$ 1.5 million + \$30 million in disposal costs + 7000 tons per day of clay disposal.	Average nickel reduction is insufficient to meet proposed limits
e) [REDACTED] Enhanced Air Floatation Filter	Not available	Not available	Average nickel reduction is

06/30/2014 - \* \* \* R2014-024 \* \* \*

			insufficient to meet proposed limits
f) [REDACTED] Lamella Gravity Settler and Sand Filter	\$6.2 million	\$2.1 million	Average Total Nickel reduction to 0.06 ppm and insufficient proposed limits
g) [REDACTED] Addition to Anaerobic Influent	Not available	Not available	Technology is not scalable. Vendor has only made multi gram quantities.

## 2 ADM Pilot trials update

As noted above ADM has completed its pilot plant trials for chemical sequestration of nickel and key cost numbers which are summarized in [Table 3](#). Detailed technical results of the pilot trials are summarized below.

### 2.1 Precipitation of Nickel

Waste Water entering the Decatur WWTP is separated into two treated, process streams: High Salt and Low Salt. Each stream is separately treated with Anaerobic and Aerobic systems. The Low Salt stream is recycled internally for water recovery and use. The High Salt stream is the primary source of nickel to SDD (Sanitary District of Decatur).

The High Salt stream must be treated to remove Nickel. The pending permit limit of 0.037 ppm is based on total Nickel. If all the precipitated nickel is removed; then, the remaining soluble nickel becomes the total nickel. To reduce and eliminate nickel from the WWTP (Waste Water Treatment

06/30/2014 - \* \* \* R2014-024 \* \* \*

Plant) stream – soluble nickel must be converted to an insoluble state; then, the challenge becomes the separation of the small amount of precipitated nickel from the large volume liquid flow.

Precipitating nickel from the High Salt stream was achieved using Nalco TX . The Nalco TX chemical and High Salt stream were combined and the reaction was time dependent – as depicted in Figure 4, the nickel solubility decreases with time. From conditions reported in Figure 4, the Nalco TX reduces the soluble nickel below 0.037 ppm; however, 100% of the precipitated nickel must be removed to achieve the limit. Longer hold times may benefit overall nickel reduction since the soluble nickel level decreases and separation of precipitated nickel efficiency will be less than 100%. A 6 MGD process will require a 250,000 gallon tank to achieve a one hour hold time.

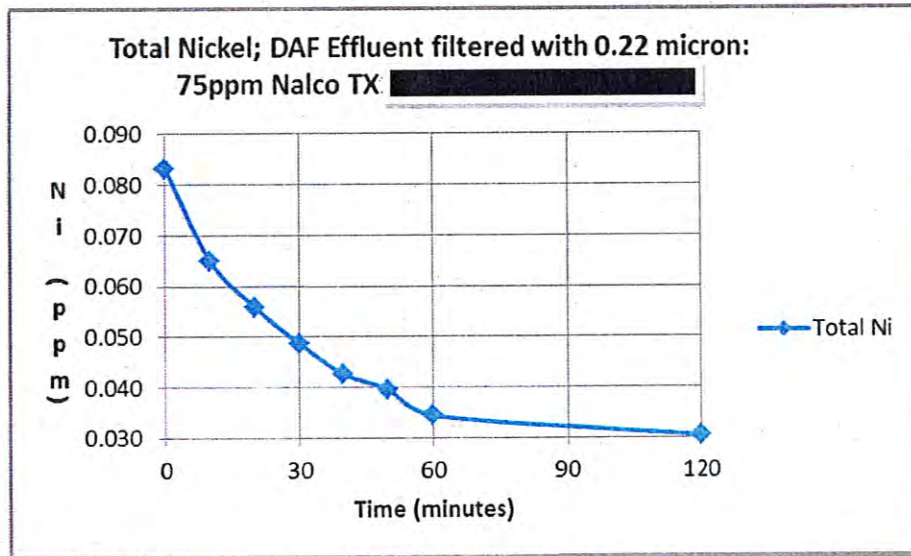


Figure 4 Maximum Nickel Reduction vs. time. After addition of metal precipitant. Starting nickel 0.083 ppm.

#### HIGH SALT INFLUENT PRECIPITATION ANAEROBIC DIGESTERS

Nickel precipitation was tested with the influent to the Anaerobic Digesters (Figure 5). Nalco TX was added to the stream, mixed in on the suction side of a centrifugal pump and sampled. Anaerobic digesters currently run a 7 day residence time. Table 4 shows the results of the experiments which demonstrate decreased soluble nickel after addition of Nalco TX. Precipitated nickel would still require removal to achieve desired nickel concentration; but, all tests reduced soluble Nickel to below 0.037

06/30/2014 - \* \* \* R2014-024 \* \* \*

ppm. This nickel is believed to become insoluble and precipitate from the solution and settle in digesters.

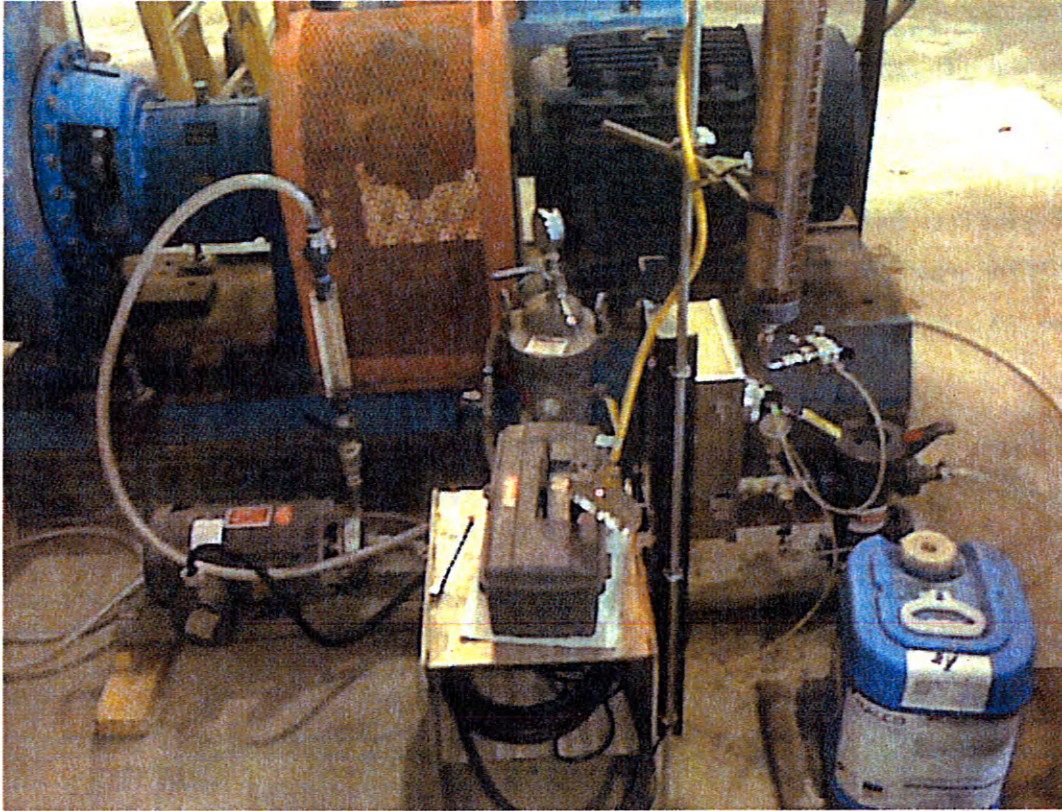


Figure 5 Nickel Precipitation skid (foreground). Nickel Precipitation of Anaerobic Digester Influent.

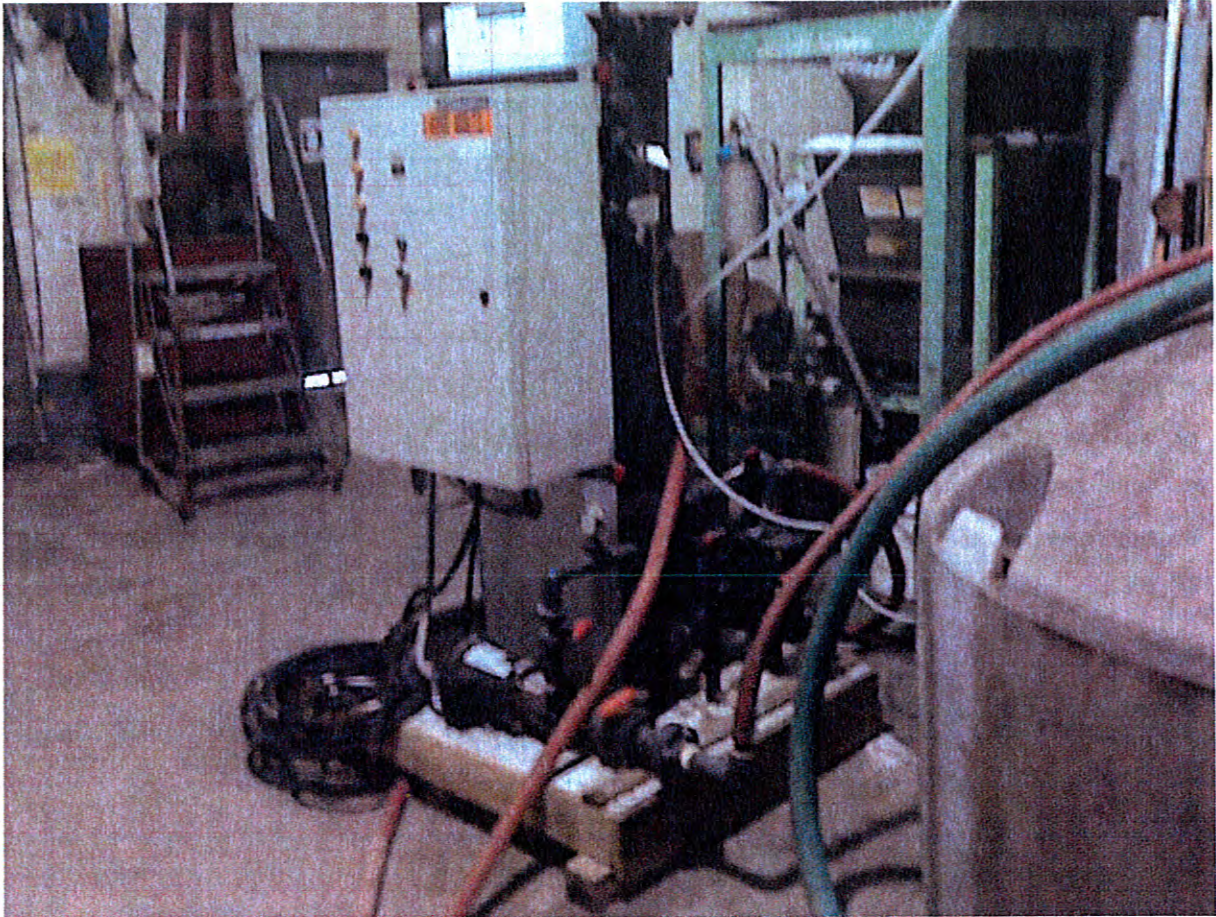
Table 4. NalcoTX addition at Anaerobic Digester. Reduction of Soluble Nickel

Sample ID	Nalco Addition	Feed Soluble Ni (mg/kg)	Product Soluble Ni (mg/kg)	Soluble Ni Reduction (%)
1	81	0.152	0.028	92
2	121	0.152	0.030	80
3	138	0.186	0.011	94
4	202	0.280	0.010	96

06/30/2014 - \* \* \* R2014-024 \* \* \*

5	274	0.152	0.026	83
---	-----	-------	-------	----

**HIGH SALT EFFLUENT STREAM; AFTER AEROBIC TREATMENT; AFTER DAF (DISSOLVED AIR FLOATATION).**



**Figure 6 Kroff Engineering/Shelton Associates – Nickel removal with Single-Pass Microfiltration**

Our tests at Kroff's, Pittsburgh, PA lab included trials of their metal precipitant process, which consists of filtration through progressively decreasing pore sized membranes, to measure the range of particle sizes that would need to be filtered. Kroff chemistry reduces soluble Nickel; but a problem remains in the separation method that removes the precipitated nickel from water- using a single pass membrane has not worked in trials.. There are some differences between the analytical results of Kroff and ADM – however both followed a similar trend of results. Kroff was only able to reduce nickel in a controlled laboratory environment.

**Table 5. Comparison of Kroff & ADM Analytic results for identical samples**

06/30/2014 - \* \* \* R2014-024 \* \* \*

	ADM Tot Ni (ppm)	Kroff Tot Ni (ppm)	Contents	Added Kroff DTC ppm	Filtered	Filter Size (micron)
1	0.024	0.003	DAF Effluent	20	Yes	0.2
2	0.043	0.025	DAF Effluent	0	Yes	0.2
3	0.066	0.038	DAF Effluent	0	No	- --
4	0.018	N.D.	DAF Influent	20	Yes	0.2

A Kroff, single-pass microfiltration skid was tested using effluent from the dissolved air flotation process (DAF) in the Decatur WWTP, DAF Effluent. A high concentration of phosphorous in the DAF effluent fouls the filter and the filtration rate rapidly decreases from twenty to less than two GPM very rapidly. Back-pulses (which are designed filter cleaning cycles) have little or no effect on this unknown substance. Kroff Engineering had tried for months to identify this contaminant without success. To provide space for screening alternate nickel filtration equipment, testing Kroff filter was terminated and equipment returned.

**GE Power & Water – Nickel Removal with EAF (Enhanced Air Floatation)**



**Figure 7 GE EAF Portable Test Skid**

We rented and tested the GE EAF unit. It was self-contained unit, built inside a shipping container and loaded onto a flatbed trailer. ADM DAF Effluent was pumped continuously, at 25 GPM, treated with Nalco TX and pumped to a holding tank for a thirty minute residence time. This treated stream was pumped to the GE EAF equipment.

Variables tested with the GE EAF unit:

1. Circulation flow rate
2. Air flow rate as well as air pressure
3. Metal precipitant dosage as well as metal precipitant brand.
4. Coagulant and Flocculent dosages

The GE EAF system was ineffective for separating the precipitated nickel. In some tests, the soluble Ni decreased below the 0.037 ppm threshold; but, the precipitated nickel would not separate using EAF.

**Table 6. EAF treated DAF Effluent.**

	Feed	EAF Product		Metal	Coagulant		Flocculent		Total Ni
	Total	Total	Soluble						

06/30/2014 - \* \* \* R2014-024 \* \* \*

ID	Ni (ppm)	Ni (ppm)	Ni (ppm)	Metal Precip	Precip (ppm)	Type	(ppm)	Type	(ppm)	Reduced (%)
16Apr	0.090	0.095	0.039	TX	500				5	-6
17Apr	0.104	0.100	0.056	TX	75				5	4
18Apr	0.101	0.094	0.044	TX	75				5	7
19Apr	0.094	0.089	<b>0.033</b>	TX	500				5	5
24Apr	0.099	0.098	<b>0.032</b>	TX	75				5	1
27Apr	0.076	0.077	<b>0.034</b>	TX	75				5	-1
4May	0.077	0.065	<b>0.027</b>	Namet	75				10	16

Alum: Aluminum Sulfate

**Parkson (Tested in Pompano Beach, FL) – Nickel removal with LGS (Lamella Gravity Settler) and Dynasand (counter-current) sand filters.**

Initial testing from Parkson Water Research Facility barely achieved 15% Ni removal. Parkson did not screen material for almost one month; so, a second sample was shipped for testing. This was tested within two days. Numerous tests were completed; of those, six tests had total nickel that was reduced below the limit. During the second session, we had six tests with product (total Ni) at, or below 0.037 ppm. After successful results, pilot equipment was sent to Decatur for further testing.

**Table 7. Total Nickel and test conditions reducing Nickel concentrations below 0.038 mg/kg. Samples from 2<sup>nd</sup> Parkson Water Research Facility Test. January 2012.**

Sample ID	Feed Total Ni ppm	Prod Total Ni ppm	Nalco ppm				Sand Filter Used	Total Ni Reduction (%)
3	0.155	0.034	50	2	2	0	N	78
4	0.155	0.037	50	0	0	100	N	76
5	0.155	0.037	50	0	2	100	N	76



06/30/2014 - \* \* \* R2014-024 \* \* \*

6	0.155	0.036	50	2	0	100	N	77
8	0.155	0.035	50	0	2	100	N	77
9	0.155	0.037	50	2	0	100	N	76

Equipment was sent to Decatur on two trucks – due to variety of reasons, the equipment was not ready to test for almost three months. Set-up required extensive use of contractors, electricians, and numerous replaced and/or new parts. The trials were finally completed towards the end of September 2012.



**Figure 8 Parkson D2 Sand Filters (Foreground on trailer)**

The flow treatment scheme required a 50 GPM flow rate; addition of Nalco TX; 30 minute hold time; Lamella; Primary Sand Filter (1.35-1.45mm) and then Secondary Sand Filter (0.85-0.95mm).

The Lamella system was ineffective at separating nickel- which was a small percentage of solids. About 40-100 ppb nickel was present in about 300 ppm of biological solids. Looking at [Table 8](#) below,

06/30/2014 - \* \* \* R2014-024 \* \* \*

reducing air flow rate through sand filters increased nickel removal. As air flow is reduced, it is postulated that precipitated nickel accumulated and formed a self-filtering media. Only one test resulted in a total nickel reduction to below 0.037ppm.

**Table 8. Parkson Results from Decatur testing of Lamella Gravity Settler and D2 Sand Filters.**

Sample ID	Feed Total Ni ppm	Lamella Total Ni ppm	Sand Filter Total Ni ppm	Nalco ppm				Air to Sand Filters SCFH	Total Ni Reduction (%)
					■	■	■		
Parkson3July-1	0.090	0.084	0.062	100	0	0	100	60	31
Parkson10July-1	0.080	0.071	0.057	50	0	1	100	75	29
Parkson11July-1	0.101	0.138	0.060	100	1	1	100	75	41
Parkson12July-1	0.087	0.065	0.050	100	2	2	100	70	43
Parkson13July-1	0.083	0.069	0.050	100	1	0	100	70	40
Prkson17July-1	0.086	0.056	0.039	200	0	1	200	60	55
Parkson18July-1	0.081	0.056	0.040	200	0	1	200	35	51
Parkson19July-1	0.089	0.071	0.037	200	0	1	200	30	58
Parkson24July-1	0.095	0.074	0.044	100	0	1	100	45	54
Parkson24July-2	0.095	0.074	0.043	100	0	1.5	100	40	55
Parkson25July-1	0.081	0.068	0.041	100	0	1	100	30	49
Parkson26July-1	0.094	0.072	0.042	100	0	1.5	100	45	55
Parkson26July-2	0.094	0.072	0.046	100	0	1.5	100	40	54

Lamella gravity settlers use gravity for the settling of the solids. However, significant problems with the Lamella were found. For example, floating solids accumulated on top of lamella during testing at Decatur WWTP. Parkson representatives traveled to Decatur and tested DAF Influent. Conclusions from testing were that Parkson does not recommend Lamella for the current ADM process. This is because the influent to current ADM DAF system is generating tiny gas bubbles that cause solids to float and the Lamella system was unsuccessful in precipitating or removing the floated solids.

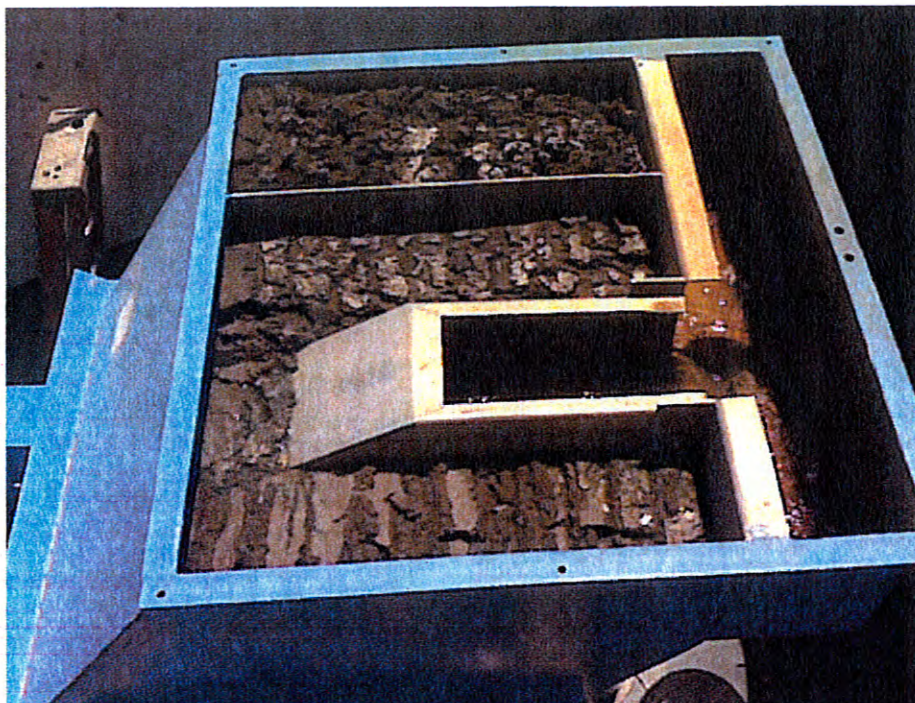


Figure 9 Solids Accumulation on top of Parkson Lamella Gravity Settler

Ecolab/Krofta Chemical Company, Inc. – Nickel removal using Dissolved Air Flootation (DAF) and Sandfloat Pilot.

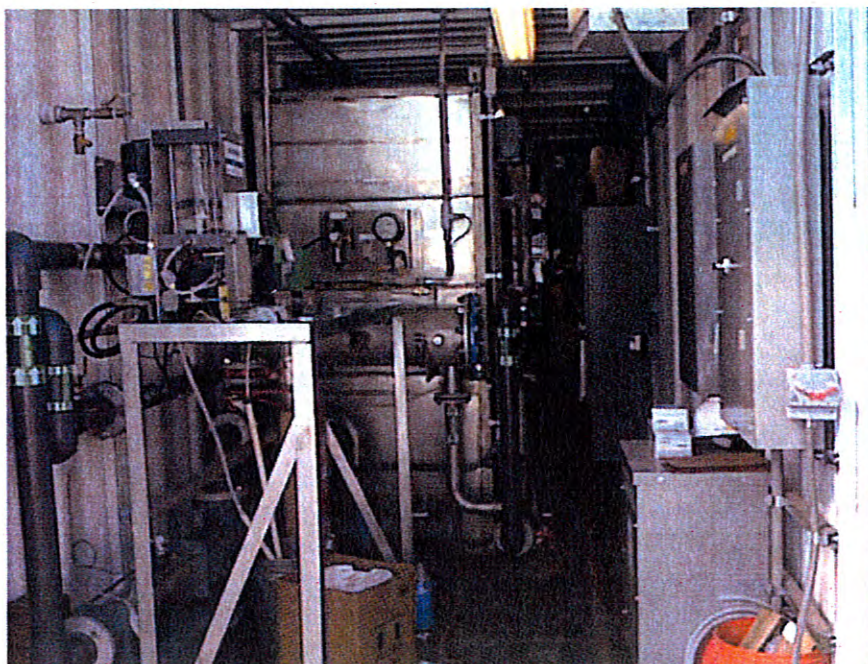


Figure 10 Ecolab/Krofta Test Skid DAF and Sand Filters

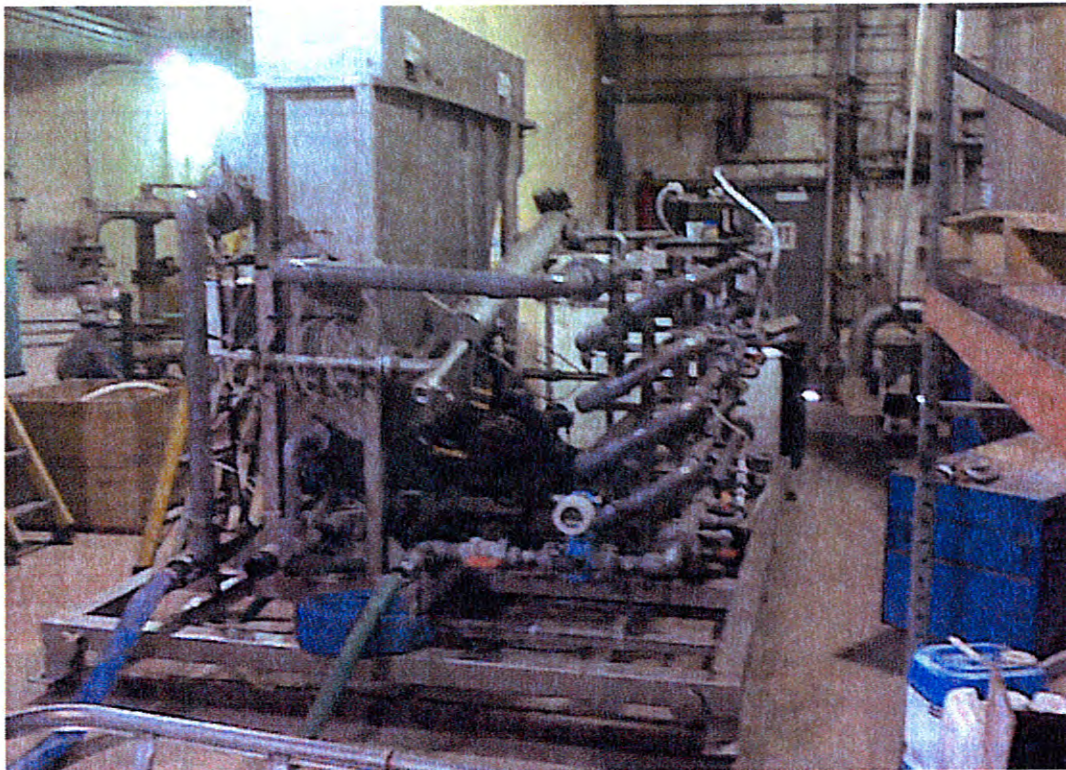
This unit contained DAF (Dissolved Air Flootation) and a sand filter. DAF removed majority of precipitated nickel. Sand Filter accounted for less than 5% of total Nickel removed. In Table 9, no operating conditions equaled or reduced nickel below 0.037 ppm.

**Table 9. Ecolab/Krofta Nickel reduction with DAF and Sand Filter**

Sample ID	Nalco Addition ppm	Feed Total Ni (ppm)	DAF Total Ni (ppm)	Sludge Recycle used	Coag Used / (ppm)	Floc Used / (ppm)	Total Ni Reduction (%)
Ecolab-1	28	0.089	0.080	No	[REDACTED]	[REDACTED]	10
Ecolab-2	28	0.067	0.068	No	[REDACTED]	[REDACTED]	(-)2
Ecolab-3	28	0.077	0.079	No	[REDACTED]	[REDACTED]	(-)3
Ecolab-4	28	0.077	0.052	No	[REDACTED]	[REDACTED]	33
Ecolab-5	55	0.078	0.055	No	[REDACTED]	[REDACTED]	30
Ecolab-6	29	0.076	0.050	No	[REDACTED]	[REDACTED]	34
Ecolab-7	61	0.075	0.052	No	[REDACTED]	[REDACTED]	31
Ecolab-10	48	0.070	0.051	No	[REDACTED]	[REDACTED]	27
Ecolab-13	48	0.071	0.050	Yes	[REDACTED]	[REDACTED]	30
Ecolab-15	48	0.073	0.055	No	[REDACTED]	[REDACTED]	25
Ecolab-18	50	0.077	0.045	No	[REDACTED]	[REDACTED]	42
Ecolab-19	50	0.081	0.066	No	[REDACTED]	[REDACTED]	19
Ecolab-20	50	0.081	0.060	No	[REDACTED]	[REDACTED]	26
Ecolab-21	50	0.081	0.079	No	[REDACTED]	[REDACTED]	3
Ecolab-22	50	0.081	0.065	No	[REDACTED]	[REDACTED]	20

[REDACTED]  
 [REDACTED]  
 [REDACTED]  
 [REDACTED]  
 [REDACTED]

06/30/2014 - \* \* \* R2014-024 \* \* \*

**FRC Systems International, LLC – Nickel removal using Dissolved Air Flootation****Figure 11 FRC Systems International DAF Skid**

This pilot was a DAF (Dissolved Air Flootation) system only. No test, using this equipment, equalled or reduced total nickel in the discharge to below 0.037 ppm. A series of experiments were performed, with FRC equipment utilizing recycled WAS (Waste Activated Sludge) achieved lower Ni levels, than similar test conditions without WAS. It was hypothesized that the WAS, may provide additional surface area, that enhances separation of precipitated Nickel. Looking at [Table 10](#), Comparing FRC-12 & 13, with FRC-14 & 15; samples using less coagulant (FRC-14 & 15) had greater total Nickel reduction – the only difference being use of recycled sludge. Comparing FRC-1 & 2; with FRC-3, 4 & 5; samples FRC-3, 4 & 5 removed more Nickel using less coagulant.

**Table 10. FRC DAF, Feed Rate ~25 GPM**

	Nalco Addition ppm	Feed Total Ni	Product Total Ni	Hold Time	Sludge Recycle	Coag Used /	Floc Used /	Total Ni Reduction

06/30/2014 - \* \* \* R2014-024 \* \* \*

		(ppm)	(ppm)	(min)	Used	(ppm)	(ppm)	(%)
FRC-1	20	0.079	0.075	30	No	██████	██████	5
FRC-2	59	0.078	0.073	30	No	██████	██████	6
FRC-3	50	0.072	0.051	30	Yes	██████	██████	29
FRC-4	50	0.072	0.053	30	Yes	██████	██████	26
FRC-5	50	0.072	0.057	30	Yes	██████	██████	21
FRC-12	50	0.074	0.059	0	No	██████	██████	20
FRC-13	50	0.074	0.065	0	No	██████	██████	12
FRC-14	50	0.074	0.048	0	Yes	██████	██████	35
FRC-15	50	0.074	0.042	0	Yes	██████	██████	43

**Alar Corp. – Nickel removal using diatomaceous earth and RVF (Rotary Vacuum Filter)**

This series of screening experiments were at the Alar Corp Facility. A bench-scale filter and Diatomaceous Earth (DE), equivalent to FW-20, was used for simulating RVF technology. As can be seen in [Table 11](#), whatever soluble Ni was precipitated – it was removed. This was the only equipment that has achieved filtrate Nickel below 0.037 ppm.

**Table 11. Alar Corp Rotary Vacuum Filtration. Various Nalco chemistries with 30 minute residence time and Medium grade DE.**

Test ID	Feed Total Ni (ppm)	Product Total Ni (ppm)	Product Soluble Ni (ppm)	Nalco TX Addition ppm	Coag Used / (ppm)	Floc Used / (ppm)	Filtration Rate Gal/ft <sup>2</sup> /Hr	Total Ni Reduction (%)
1	0.070	0.026	0.026	50	██████	██████	22	63
2	0.070	0.027	0.026	50	██████	█	27	61
3	0.070	0.028	0.027	50	██████	█	28	60
4	0.070	0.028	0.027	50	██████	██████	23	60
5	0.070	0.028	0.028	25	██████	██████	26	60

06/30/2014 - \* \* \* R2014-024 \* \* \*

6	0.070	0.028	0.027	25	██████	██████	24	60
7	0.070	0.028	0.027	25	██████	█	27	60
8	0.070	0.029	0.027	25	██████	█	42	59
9	0.070	0.031	0.028	75	██████	█	39	56
10	0.070	0.035	0.034	75	██████	██████	26	50

Previous testing at Decatur WWTP incorrectly assumed the thirty minute residence time, after metal precipitant addition, was unnecessary. The majority of tests (see [Table 12](#), next page) did not remove precipitated nickel. The primary reason for omitting the thirty minute hold is that the bottom four rows of [Table 12](#) incorporate the 30 minute residence time. Soluble and Total Nickel numbers are similar, indicating that almost all the precipitated nickel has been filtered. Medium grade DE (FW-20) also appears to be necessary for removal of precipitated nickel. Coarse grade DE had higher filtration rates, but Nickel separation was lower.

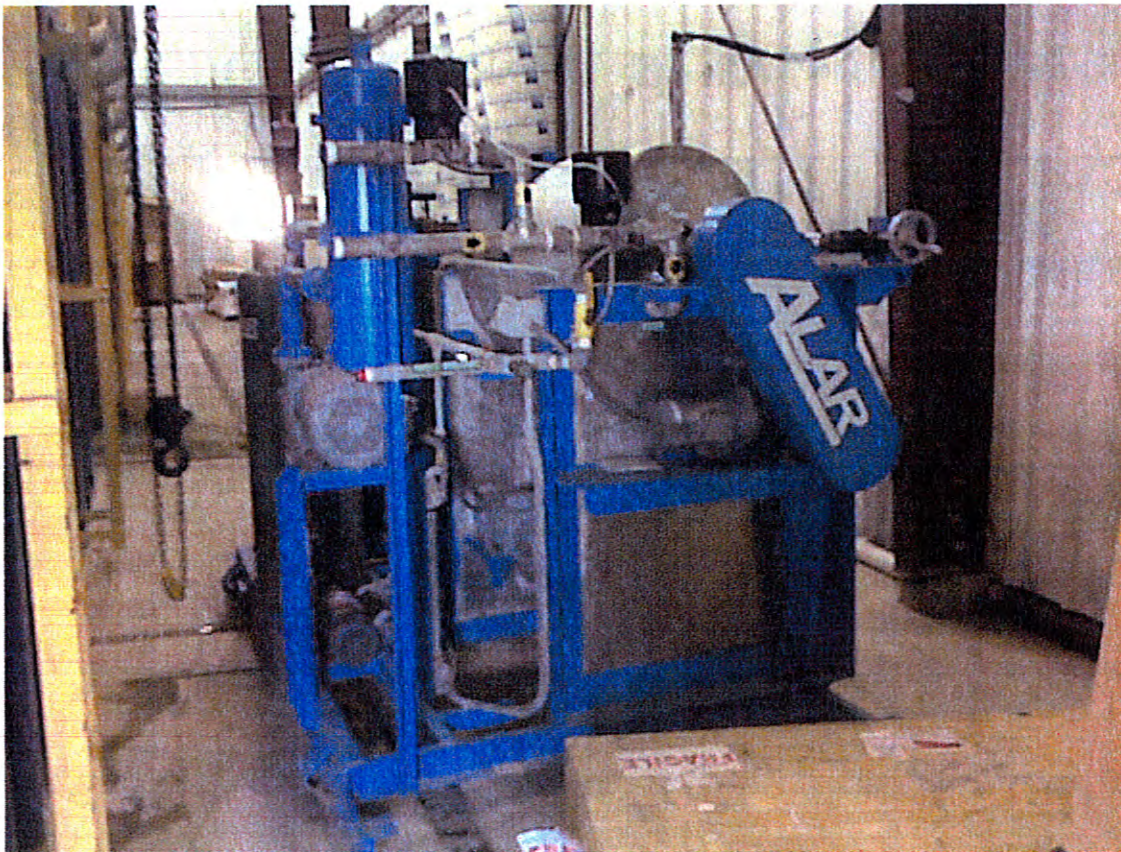


Figure 12 Alar Corp Rotary Vacuum Pilot Skid

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Table 12. ALAR RVF. Screening: metal precipitant, Coagulant, with and without 30 minute hold after adding Metal precipitant. Tests with the 30 minute residence time, after Nalco TX addition, are in bold font.**

Sample ID	Feed Total Ni (ppm)	Product Total Ni (ppm)	Product Soluble Ni (ppm)	Metal Precipitant		Coagulant		Feed	D E	Filtrate Rate Gal/Hr/Ft <sup>2</sup>	Total Ni Reduction (%)
				Brand	ppm	Brand	ppm				
05Mar-1	0.081	0.068	0.066	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	39	16
05Mar-2	0.083	0.044	0.033	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	31	47
06Mar-1	0.085	0.046	0.044	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	37	46
07Mar-1	0.079	0.051	0.050	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	40	35
08Mar-1	0.079	0.050	0.050	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	37	37
09Mar-1	0.079	0.050	0.028	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	32	37
12Mar-1	0.073	0.060	0.025	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	42	18
16Mar-1	0.083	0.073	0.020	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	42	12
19Mar-1	0.088	0.072	0.049	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	C	42	18
19Mar-2	0.086	0.070	0.060	<b>■</b>	<b>■</b>	<b>■</b>	<b>■</b>	Eff	M	42	19



20Mar-1	0.085	0.074	0.037	█	█	█	█	Eff	C	39	13
20Mar-2	0.086	0.073	0.035	█	█	█	█	Eff	M	33	15
21Mar-1	0.085	0.073	0.035	█	█	█	█	Eff	C	50	14
21Mar-2	0.082	0.073	0.033	█	█	█	█	Eff	M	33	11
22Mar-2	0.083	0.069	0.033	█	█	█	█	Eff	C	39	17
03Apr-1	0.095	0.055	0.045	█	█	█	█	Eff	C	46	42
10Apr-1	0.099	0.044	0.042	█	█	█	█	Eff	M	46	56
11Apr-1	0.094	0.042	0.039	█	█	█	█	Eff	M	33	55
11Apr-2	1.16	0.045	0.042	█	█	█	█	In	M	3	96

Average DAF Effluent Feed: 0.084 ppm total Ni; 0.081 ppm Soluble Ni

Average DAF Influent Feed: 0.828 ppm total Ni; 0.098 ppm Soluble Ni

█  
 █  
 █  
 █

Sanitary District of Decatur (SDD) collected influent and effluent samples, three times per week, beginning in January 2012. Assuming the Sanitary District of Decatur, Waste Water Treatment Plant is removing precipitated Nickel during routine handling.

Table 13: Average Results from January 2012 SDD samples.

	Soluble Ni (ppm)	Total Ni (ppm)
--	------------------	----------------

06/30/2014 - \* \* \* R2014-024 \* \* \*

SDD Influent	0.025	0.078
SDD Effluent	0.023	0.024

## 2.2 Membrane Filtration

### Salt Creek Tech: Hollow Fiber Membrane Filtration.

Salt Creek Tech equipment was in Decatur on a bench-scale; the equipment consisted of a hollow-fiber membrane filter. Tests with the hollow-fiber membrane achieved Nickel levels below permit limit, if Aluminum Sulfate (Alum) and Nalco TX were added to the feed, before processing. Screened solids had nickel removed, however no flux data was shared by the vendor on the bench top trials.

**Table 14. DTC 75ppm Nalco; 300ppm Alum; 30 minute residence time; Samples processed with Hollow Fiber filter**

Sample Name	Total Ni	Total Ni	Soluble Ni	Soluble Ni
	(ppm)	Reduced (%)	(ppm)	Reduced (%)
Untreated Feed	0.080		0.077	
Alum/DTC treated feed	0.054	33	0.025	65
Alum/DTC treated perm	0.017	79	0.015	78
Alum treated Feed	0.076	5	0.067	13
Alum Treated Perm	0.055	31	0.055	28
Raw Material Feed	0.071	11	0.069	10
Raw Material Perm	0.042	48	0.039	48

### ADM: Membrane Filtration

ADM trialed a hollow fiber membrane module to evaluate the approach from Salt Creek Technology. Starting material for ADM test was identical to Alum/DTC treated DAF Effluent used with the lowest nickel results from Salt Creek Tech. ADM started the test and allowed the experiment to run for ~5 hours. Sampled and measured permeate results are in [Table 15](#) below. Flux after one hour: 17.5 L/Hr/m<sup>2</sup> (0.43 gal/Hr/ft<sup>2</sup>)

06/30/2014 - \* \* \* R2014-024 \* \* \*

**Table 15. 75ppm Nalco TX300ppm Alum; 30 minute residence time; Test Filter: Pall USP-143 Hollow Fiber Module.**

Sample ID	Flux L/Hr/m <sup>2</sup>	Flux Gal/Hr/ft <sup>2</sup>	Total Ni (mg/kg)	Soluble Ni (mg/kg)	Total Ni Reduction (%)
Feed	N.A.	N.A.	0.102	0.082	---
10 min	N.A.	N.A.	0.020	0.021	80
60 min	17.5	0.43	N.A.	N.A.	---
140 min	11.8	0.29	0.021	0.020	79
290 min	8.5	0.21	0.020	0.020	80

### 2.3 Proprietary adsorbent

As part of continuing effort to screen Nickel removal technologies – ADM contacted [REDACTED], a start-up company, based in Lafayette, CO. Themedia is proprietary - a granular carbon based support, impregnated with ligands. Very preliminary results reported in [Table 16](#). This test, completed at Tusaar, used ADM DAF Effluent, pumping 0.4 mL/min through 4.0 g of Tusaar media. The sample listed on the bottom row of [Table 16](#), was obtained after ~4 liters DAF Effluent had passed through the media – which would be approaching 450 bed volumes of treated liquid. All samples processed with this media have been below 0.037 ppm total Nickel. ADM and Tusaar are discussing next steps for pilot planning.

**Table 16. Selected Results of DAF Effluent treated at 0.4 mL/min through 4.0 grams of [REDACTED] Media.**

	Feed Total Ni (ppm)	Product Total Ni (ppm)	Total Bed Volumes Processed (estimated)	Total Ni Reduced (%)
[REDACTED]	0.096	0.002	67	98
[REDACTED]	0.096	0.006	124	94
[REDACTED]	0.096	0.010	180	90
[REDACTED]	0.096	0.012	236	87
[REDACTED]	0.096	0.014	292	85

06/30/2014 - \* \* \* R2014-024 \* \* \*

	0.096	0.014	348	85
	0.096	0.015	449	84

## 2.4 Other approaches

### GEM (Gas Energy Mixing)

In April 2012, ADM traveled to Clear Water Technology for an equipment demonstration. This technology utilizes a series of six, LSGM (Liquid Solid Gas Mixers) "heads" allowing different points of injection and mixing. Mixing streams (chemical precipitant, coagulant, flocculent) are added tangentially, to a vertical pipe, very much like a hydroclone. The two-phase system operates at 100-120 psi, with a variable amount of pipe filled with air. A thin liquid film circulates around the inside of pipe. Mixing energy is controlled by adjusting the port size, the number of ports/injection points and the levels inside pipe. Mixing energy can be adjusted:

1. to prevent overmixing
2. Uncoil long molecular chains, exposing more/all charge sites to particles.

Through the six LSGM heads, air is dissolved into waste water, prior to formation of floc – the dissolved air essentially becomes part of the floc structure once it is formed. As stream depressurizes and enters the floatation tank, air bubbles expand and push out water from the floc – making a very buoyant, drier sludge. Formation of air bubble and floc nucleation occur simultaneously. Examples at the Clean Water Technology showroom were still buoyant years after test were completed. The estimated test costs from March 2012 were \$38,367

Additionally we have plotted a summary of all soluble nickel reduction achieved as a function of the incoming nickel concentration in DAF effluent. As is evident we are not seeing a consistent reduction to below 0.037 ppm.

06/30/2014 - \* \* \* R2014-024 \* \* \*

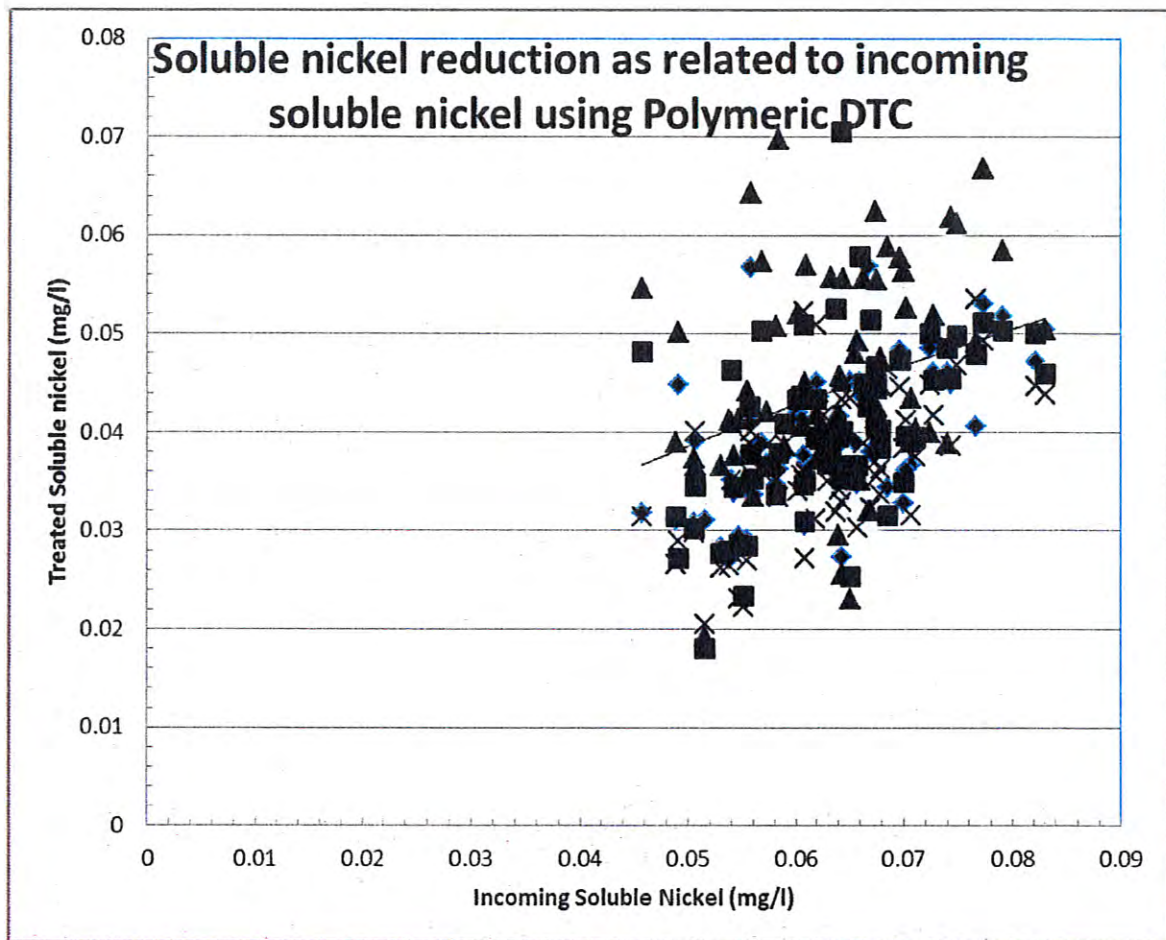


Figure 13 Soluble nickel reduction in Decatur complex effluent

## 2.5 Toxicity trials

### River Bend Labs

Anaerobic Tox test for Nalco TX at: 0.01, 0.1, 1.0 10.0, & 100.0 ppm

Starting material for this test was Decatur High Salt Anaerobic Influent. This was tested at River Bend Labs (St Charles, MO). Summarizing River Bend results: Increasing the concentration of TX had no effect on Anaerobic Digesters. Gas production varied across every concentration; but, in general, all tests followed the same trend and were not statistically different.

Respirometry Test for:

1. mixed liquor city influent (control)
2. ADM DAF effluent
3. ADM DAF effluent, treated with ALAR RVF and mixed liquor (city)

06/30/2014 - \* \* \* R2014-024 \* \* \*

River Bend Results: All tests behaved identical to control. The material seems to not be toxic to Heterophilic bacteria at the city of Decatur.

Nitratox Test for:

1. Control DI water
2. City of Decatur Influent
3. 40% City of Decatur Influent; 60% ADM DAF Effluent
4. 40% City of Decatur Influent; 60% ADM DAF Effluent treated through the ALAR RVF.

River Bend Results: Nitrification inhibition occurred on all samples but the DI water control. This points to something inhibiting on the city influent to nitrification.

### 3 Corn Plant used IX system

As previously disclosed, ADM has been working to install a used ion exchange resin bed system to capture Nickel leaching from the sorbitol process catalyst. This system ran manually for 6 weeks in late 2011. Thus far, about 5 lbs of Nickel have been removed from the treated stream and no Nickel has been detected in the effluent. This is shown in [Figure 14](#). We are using 105 cu ft of resin and expect a Nickel binding capacity of about 3.4 lbs per cubic ft.

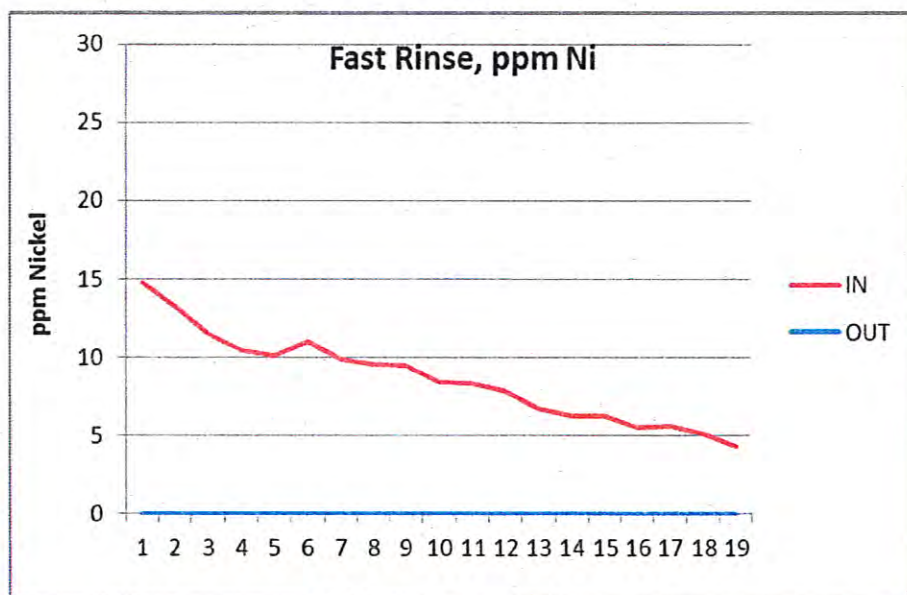
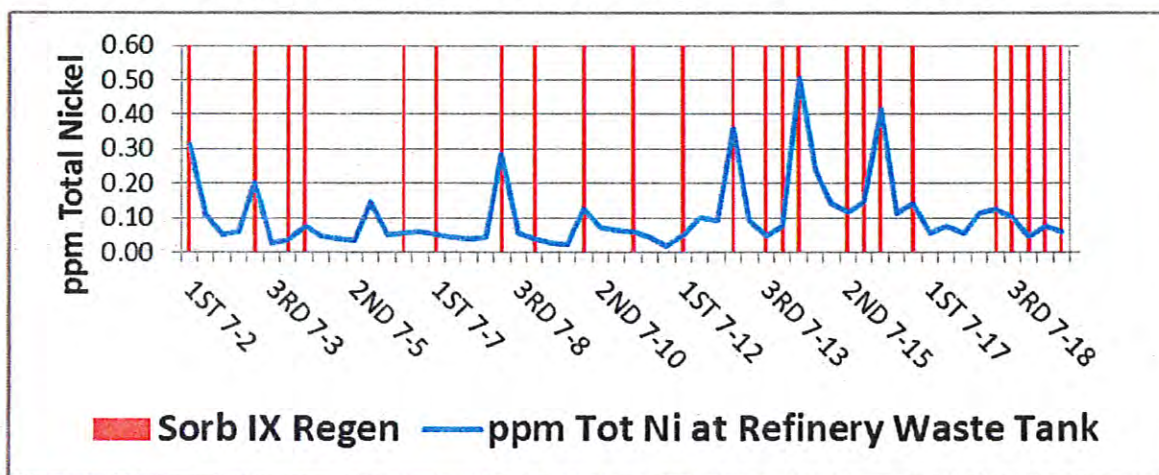


Figure 14 Used ion exchange resin treating material leaving the sorbitol process

The IX units went into continual operation in early 2012 and performance degraded by spring of 2012. In addition, a leak was discovered in a Mott sintered filter. Check filters were brought on line prior to IX in case this happens again.

06/30/2014 - \* \* \* R2014-024 \* \* \*

No progress had been made by summer of 2012 in pin-pointing the cause of the performance problems. In July, we began employing continuous Isco samplers. [Figure 15](#) illustrates the erratic performance.



[Figure 15 Nickel losses to WWTP during Sorbital IX regenerations](#)

An Isco sampler was moved to the Nickel bed inlet, but the source of the problem still could not be identified. The vessels weren't set up to sample the common outlet, so piping modifications were made in mid-November 2012. This will allow two Isco samplers to be used directly at the inlet and outlet of the beds. A new round of sampling began the week of 11/26/12.

#### 4 [Review Ceased for Technologies](#)

Since the summer 2012 update, we have completed all planned pilot trials. At present, we continue to monitor our effluent discharges and update the SDD. No additional pilot trials are planned at this time.

#### 5 [Polyols IX waste stream treatment](#)

We have identified our Polyols ix waste stream (between 16-22% of total Nickel load) as a significant contributor of inorganic Nickel due to corrosion of our distillation columns. Initial work using high pH precipitation has shown almost a complete removal of soluble Nickel.

Initial work suggests a pH modification would eliminate all soluble Nickel from the IX regen streams with chemical costs about \$300 per day. We have performed additional testing with 3M using cartridge filters for sizing of plant equipment. Capital expenditures for the plant system are estimated at \$450,000. [Figure 16](#) is the layout of the proposed nickel removal system at Polyols. We expect the system to be installed in 2013 pending regulatory and environmental approvals.

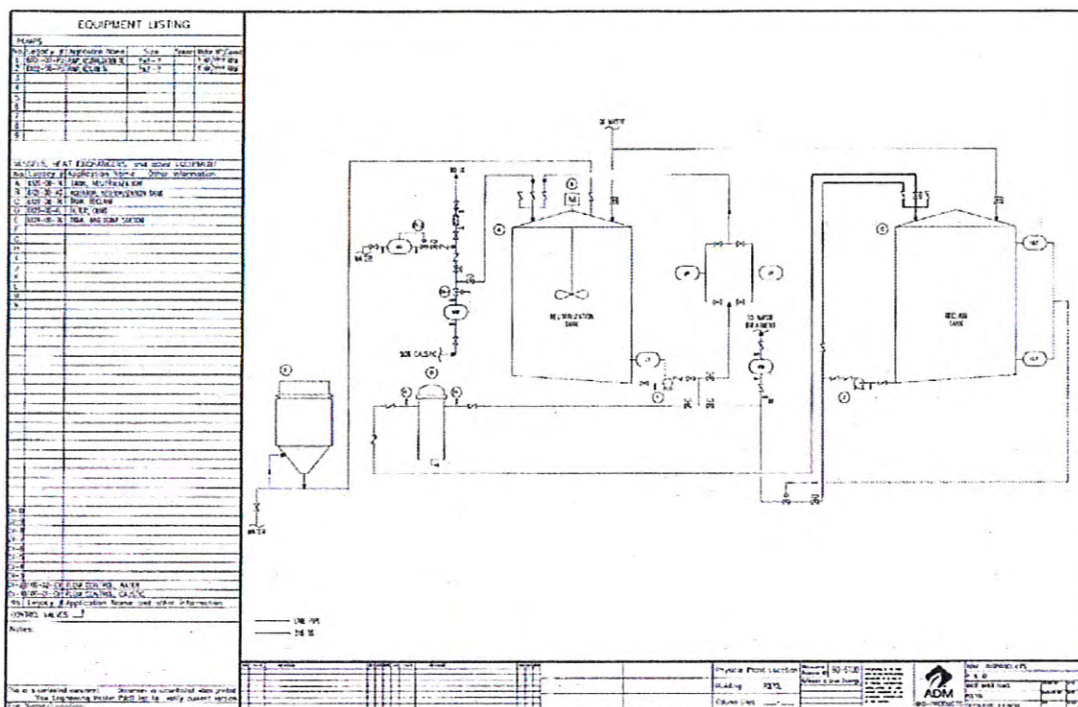


Figure 16 [Redacted]

6 Respirometer and Nitratox Testing

Results from Respirometer and Nitratox testing of Decatur Sanitary Districts MLSS using Nickel reduction chemistries piloted at ADM was shared with the district in May 2012. No additional tests were conducted as all the chemistries being piloted successfully passed the district’s requirements on residual ammonia and respirometer performance.