

**BEFORE THE ILLINOIS POLLUTION CONTROL BOARD**

IN THE MATTER OF:	)	
	)	
WATER QUALITY STANDARDS AND	)	
EFFLUENT LIMITATIONS FOR THE	)	
CHICAGO AREA WATERWAY SYSTEM	)	R08-9(D)
AND THE LOWER DES PLAINES RIVER:	)	(Rulemaking-Water)
PROPOSED AMENDMENTS TO 35 ILL.	)	
Adm. Code 301, 302, 303 and 304	)	

**NOTICE OF FILING**

To: John Therriault, Clerk  
 Illinois Pollution Control Board  
 James R. Thompson Center  
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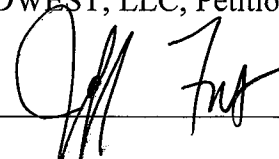
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**SERVICE LIST**

Please take notice that on November 22, 2013, we filed electronically with the Office of the Clerk of the Illinois Pollution Control Board the attached **Pre-Filed Testimony of: Larry Tyler, Bruce Nelson, Roger Klocek and James Huff**, a copy of which is served upon you.

CITGO PETROLEUM CORPORATION and  
 PDV MIDWEST, LLC, Petitioners

By:  \_\_\_\_\_

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Adm. Code Parts 301, 302, 303 and 304 )

**PRE-FILED TESTIMONY OF JAMES E. HUFF, P.E.**

**Introduction**

My name is James E. Huff, and I am Vice President and part owner of Huff & Huff, Inc., an environmental consulting firm founded in 1979. I previously testified in this rulemaking on May 6, 2009 and again on October 8, 2010, prior to the division into sub-dockets. A copy of my background was summarized in the pre-filed testimony that accompanied my May 6, 2009 appearance.

I have been retained by the Citgo Lemont Refinery (“Lemont Refinery” or “Refinery”) to review the proposed water quality standards proposed by the Illinois EPA (the “Agency”) for Use B waters, or specifically the Chicago Sanitary & Ship Canal downstream of the Calumet-Sag Channel confluence (the “Lower Ship Canal”) and the technical justification provided by the Agency in support of its proposed water quality standards. I have actively followed the UAA proceedings before the Board. I have also evaluated the impact that the proposed use designation will have on the Lemont Refinery. My prior testimony focused on the uses of the Ship Canal and voiced concerns over the proposed chloride, sulfate, and mercury water quality standards. My testimony today expands on these concerns and provides additional insight on alternative regulatory approaches that the Board might consider.

The Lemont Refinery discharges into the Lower Ship Canal. At the point of its discharge, the Lower Ship Canal can be described - as the Agency has stated - as an “effluent dominated” waterway. The Lemont Refinery discharges directly into the *Regulated Navigation Area* (“RNA”) associated with the electric barrier, and the Refinery’s mixing zone extends into the electric barrier *Black Safety Zone*, where fish would be expected to be non-existent.

**USEPA's Involvement With Respect to Board Granted Variances**

Historically the Illinois Pollution Control Board has issued variances where compliance would impose an arbitrary or unreasonable hardship, under the criteria of the Illinois Environmental Protection Act. One question routinely asked is whether the relief is consistent with federal law. As the Board is aware, the Lemont Refinery, in order to install a wet gas scrubber to remove sulfur dioxide under a USEPA consent order, a variance was sought from the Board to exceed the 1,500 mg/L Total Dissolved Solids (TDS) water quality standard. The variance route was recommended by the Illinois EPA and they supported the variance. The variance was necessary because the Ship Canal upstream of the Lemont Refinery exceeds 1,500 mg/L TDS during snow melt periods from de-icing practices throughout Northeast Illinois. As a result of the delay in adopting revised water quality standards in these proceedings, the Lemont Refinery has sought two extensions, which the Agency supported and the Board approved. In each of these three variances, both the Lemont Refinery and the Agency stated their belief that the relief was consistent with the Clean Water Act.

USEPA formally objected to the Lemont Refinery's draft NPDES permit in March, 2013. USEPA has stated that all variances involving water quality standards must be approved by the USEPA and must comply with 40CFR131.10(g). The criteria in 40CFR131.10(g) are the same criteria which are being applied to the UAA proceedings. Given that the Agency already determined in this rulemaking that it thought the Ship Canal qualified for not just one, but for three of the factors under 131.10(g), the USEPA objection came as a surprise to the Lemont Refinery. There seems to be a new set of issues that must be kept in mind in adopting water quality standards. In this proceeding, Docket D, the Board is to set the water quality standards that reflect the uses. For the Lower Ship Canal it is Aquatic Life Use B. My colleague Roger Klocek is providing specific testimony on the issue of water chloride toxicity to the aquatic species present in this Use B designation in this rulemaking. It remains to be seen if the same kind of detailed analysis is going to be necessary and even sufficient to meet future USEPA scrutiny for water pollution variances. As I have learned from both the Lemont Refinery work I have done and for other dischargers, on a site specific basis, such as in a variance under Illinois law, it can

be very difficult to satisfy those conditions of 40 CFR 131.10(g) under USEPA's interpretation.

It is also disconcerting that the USEPA somehow has tied the Lemont Refinery's wet gas scrubber and the associated sulfate discharge to a concern over chloride toxicity. Before the Board adopts new water quality regulations, it should consider carefully the economic feasibility and technical reasonableness of these proposed standards, particularly given the unique conditions of the Ship Canal, including the effluent dominated nature of the waterway as well as the presence of contaminated sediments. Adopting the proposed water quality standards comes at a significant cost. Indeed, those costs would be borne by entities located on the Ship Canal, a commercial and industrial corridor that is well suited for hosting such operations. We need to be more creative on how we address the environmental concerns associated with chlorides and mercury. My testimony will offer one such alternative.

**TMDLs take a long time and in the meantime IEPA imposes the WQS as permit effluent conditions**

I would urge the Board to be cautious before adopting any proposed water quality standard when it is known that the stream currently violates that proposed standard. The proposed water quality standards for mercury and chlorides are serious problems for affected dischargers.

If a receiving stream exceeds a water quality standard, then it is put on the "303(d) list" by the Agency. Once on the list, the stream segment is supposed to go through a process by which a "Total Maximum Daily Load" limit is established for that water body. However, the 303(d) process is lengthy. For example, there are over 2,000 listed impairments in the 2014 303(d) list, within approximately 500 stream reaches. There are only 79 impairments on the 2014-2016 schedule for TMDL development. Only three TMDLs were finalized in the last two year cycle. None of those on the list for the next two years deal with the waters involved in this UAA process and only one planned

TMDL (Drowning Fork) is directed at chloride impairment. While the Ship Canal and other CAWS waters are on the 303(d) list and a couple are listed for TDS impairment, all are listed as "low priority." I would therefore expect that if the Board adopts the chloride and mercury water quality standard as proposed by the Illinois EPA, a TMDL would not be completed for years. Based on my permitting experience and with the mixing rule, IEPA would begin to impose an effluent limit equal to the water quality standard, even where the discharger is a very minor source of the pollutant and upstream dischargers are causing the exceedance of the water quality standard. That is why the Lemont Refinery sought a TDS variance in 2005 for the wet gas scrubber installation per the USEPA consent order. A variance from the Board is no longer enough, as now USEPA is intimately involved. But getting a variance from USEPA, even after getting a variance from the Board, has proven difficult at best.

#### **Mercury Water Quality Data**

The Lemont Refinery withdraws water used for processing from the Ship Canal at river mile 296.8. In the summer of 2008 and again in 2011, Huff & Huff, Inc. was asked to conduct metals sampling at the intake, including mercury sampling using USEPA's Ultra Clean Sampling Protocol Method 1669.

Attachment 1 includes the mercury results from the Ship Canal, collected upstream of the Lemont Refinery discharge. While the dissolved mercury levels were low, the total mercury averaged 9.59 nanograms per liter (ng/L). For four out of the twenty sample dates, flow was above the harmonic mean and the total mercury exceeded 12 ng/L, or 20 percent of the time. Four of the six samples collected during periods of Ship Canal flows above the harmonic mean exceeded the 12 ng/L proposed standard. In other words, 67% of the time of high flows, there was an exceedance of the proposed standard. The exceedances are likely caused by re-suspension of sediment during higher flow periods. Based on the proposed rule 302.407 (c) and (e), these events would be a violation of the proposed mercury water quality standard. Even though a discharger like the Lemont Refinery has nothing to do with stream flows above the harmonic mean nor with the re-suspension of contaminated sediments, as I understand the Agency's policies, because the

water quality upstream of the Lemont Refinery exceeds the proposed water quality standard, the Refinery would not be allowed a mixing zone for mercury.

The acute and chronic mercury water quality standards are readily being achieved, as presented in Attachment 1. There is no fishing permitted in the RNA or the Safety Zone, yet the proposed standard for mercury, which assumes fish consumption by humans, would be violated due to existing sediment contamination.

If the stream already exceeds the proposed water quality standard, then mercury would be listed as a cause of water quality impairment on this waterway. It is my understanding under the Clean Water Act, that EPA is then required to conduct a TMDL study; however, if history is any guide, the Illinois EPA would simply begin issuing NPDES permits with a 12 ng/L annual average effluent mercury limit to dischargers to the Chicago Area Waterways. It is clear the source of the mercury at high flows is primarily from re-suspended sediment, and imposing the point source effluent limits will have little-to-no effect on the existing mercury concentrations in the Chicago Area Waterways. Before adopting a 12 ng/L mercury water quality standard for Use B waters, the Board should consider the implications of such an action. A TMDL study on the mercury would likely recommend either dredging of the Ship Canal or prohibiting fishing on Use B waters, not simply imposing a 12 ng/L effluent permit limit on dischargers. There already is no fishing permitted in the RNA.

The influent total mercury to the Lemont Refinery from samples collected in 2008 and 2011 averaged 9.59 ng/L. Using the harmonic mean flow in the Ship Canal, 55 pounds per year of mercury pass the Lemont Refinery. The Lemont Refinery's net mercury contribution is 0.075 pounds per year, or 0.14 percent of the total mercury loading.

#### **Chloride Water Quality Data**

Attachment 2 presents eight years of winter chloride data from the Lemont Refinery's water intake. Summer time chlorides are consistently well below the proposed 500 mg/L chloride water quality standard. Winter chloride levels as high as 1,099 mg/L have been recorded at the Lemont Refinery intake. The chloride level in the Ship Canal has

remained above 500 mg/L for over three weeks at a time, such as from January 28, 2008 to sometime between February 16 and 18, 2008. Chloride concentrations above 500 mg/L occur nearly every winter. The intense population center (i.e. the City of Chicago and suburban Cook County which are upstream of the Lemont Refinery) on an effluent dominated stream like the Ship Canal make achieving a 500 mg/L chloride standard not practicable without changing de-icing practices upstream of the Lemont Refinery.

When EPA undertakes a TMDL study for chlorides on the Ship Canal, it would identify the sources of chlorides and determine the most cost effective way to achieve the water quality standards, if technically feasible. (Similar to what is supposed to happen with mercury.) Flow augmentation using a portion of the MWRDGC's discretionary diversion from Lake Michigan for these 18.36 days per year would be a logical outcome of such TMDL study for chlorides. MWRDGC already uses such diversion for low dissolved oxygen in the summer months, and the feasibility of using some of this flow for maintaining the chloride standard in the winter months should be investigated.

The Lemont Refinery has a draft NPDES permit that has imposed a 1,500 mg/L TDS **effluent** limit on the Refinery whenever the Ship Canal is over 1,500 mg/L TDS, before any TMDL has even been attempted. The TDS limit was imposed due to the sodium chloride spikes from winter snow melt.

If the Agency's proposed 500 mg/L chloride standard is adopted, based on the draft NPDES for the Lemont Refinery, a 500 mg/L effluent chloride limit would become routine for the point source dischargers on the Chicago Area Waterways, preceding any TMDL study. Facilities that use once through cooling water would not be allowed to add chlorine (increase in chlorides) to control microbial growth at least during the periods that Chicago Area Waterway is over 500 mg/L chlorides. On an effluent dominated stream, chlorinating the incoming water is important to prevent biological growth on the heat exchangers. To discontinue discharging would entail ceasing operations for most industries, which has its own economic ramifications. In addition, new dischargers to the Ship Canal would essentially be limited to operations that did not add any heat (no once through cooling), chlorinate, use de-icing salt in the winter, or any process that

contributes chlorides. MWRDGC would also not be allowed to discharge during periods its effluent exceeded 500 mg/L chlorides, which would occur when the Chicago Area Waterways are over 500 mg/L.

As noted previously, with USEPA's current position, variances in Illinois where a water quality standard is exceeded may be quite difficult. If the Board adopts the proposed chloride standard, there will be severe hardships on all discharges to the Chicago Area Waterways.

**Chloride Mass Balance**

I have mentioned highway de-icing salts as the cause of the chlorides exceeding 500 mg/L in the winter months, and the need to complete a TMDL study before imposing effluent limits on chlorides. The Illinois State Water Survey in 2012 issued a report entitled *The Sources, Distribution, and Trends of Chloride in the Water of Illinois*, selected excerpts of which are included as Attachment 3 to my testimony. The annual contribution from various sources is presented in Table 1 of Attachment 3, and the highlights are as follows as they relate to the Chicago Area Waterways:

Source	Chlorides, Tons/yr
Treated Wastewater	
MWRDGC	<b>192,000</b>
Remainder of State	<b>138,000</b>
Road Salt	<b>518,000</b>
Water Conditioning Salt	<b>148,000</b>
Fertilizer (KCl)	<b>410,000</b>
Lake Michigan Withdrawals	<b>37,000</b>
Groundwater withdrawals Aggregate	<b>31,000</b>

a/ Report presents data in metric tons of chlorides, converted to short tons

The Illinois State Water Survey report found that highway de-icing salts are the largest single source of chlorides being introduced into our environment, followed by potassium fertilizer. The report found that the road salt is primarily associated with the urban areas, which of course would be the Chicagoland area that is primarily upstream of the Lemont Refinery, and would include the MWRDGC discharges as well as separate storm sewers



throughout the region. It is clear that literally hundreds of thousands of tons of chlorides per year are discharged into the CSSC upstream of the Lemont Refinery.

Focusing on the Lemont Refinery, one can compute what its contribution to the total chloride loading is on the Ship Canal. Attachment 4 is a computation of the chloride in the Refinery's intake and effluent, as well as what is flowing through the Ship Canal. During times when the Ship Canal exceeds the proposed 500 mg/L chloride water quality standard, the Lemont Refinery contributes less than 0.18% of the total chloride loading. It should be noted that the vast majority of the year, there is sufficient assimilative capacity in the Ship Canal to handle the Lemont Refinery outfall without exceeding 500 mg/L chlorides at the edge of the mixing zone.

From the Ship Canal monitoring, the chlorides are above 500 mg/L an average of 18.36 days per year. Attachment 5 calculates the Lemont Refinery's contribution above 500 mg/L chlorides during these 18.36 days per year. The result is the Refinery is currently contributing 119 tons per year of chlorides to the Ship Canal when there is no assimilative capacity. I will discuss this contribution further in a moment, together with a proposal to mitigate the environmental and economic harm that the proposed standard would cause.

### **Mixing Zone Implications**

The Illinois mixing zone regulations are found in 35 Ill Adm Code Section 302.102. Section 102(b)(9) does not allow for any mixing zone for a constituent where the water quality standard is violated. The Lemont Refinery's draft NPDES permit allows for a mixing zone for Total Dissolved Solids (TDS), except when the Ship Canal exceeds 1,500 mg/L TDS. The Lemont Refinery completed a mixing zone study in 1992 that found the Zone of Initial Dilution (ZID), 10:1 dilution of the effluent and a mixing zone that only extended 380 feet downstream and provided a 60:1 dilution. With the higher flow today in the effluent, the mixing zone extends 570 feet downstream before it can no longer be tracked. The Agency has utilized this study when deriving water quality based ammonia effluent limits. Exhibit A to the testimony of Larry Tyler depicts the current

Lemont Refinery mixing zone, which starts within the RNA and extends into the Black Safety Zone, both associated with the electric fish barrier. At the edge of the mixing zone, changes from upstream concentrations cannot be measured. Despite the inability to detect any change in the chloride, TDS, and mercury at the edge of the mixing zone, the loss of this mixing zone is very problematic, as the Lemont Refinery, and all other dischargers on the Ship Canal, will have water quality standards imposed as effluent standards. It should be further noted that from Mr. Scott Twait's testimony at the previous hearing, it is unclear exactly what the Agency's position on mixing zones for mercury on the Chicago Area Waterways, and the Board has an opportunity to clarify this confusion.

**Economic Impact of the Chlorides and Mercury Proposed Water Quality Standards on the Lemont Refinery**

The Lemont Refinery has been an active participant throughout these proceedings. There are certainly a number of other industrial and municipal dischargers that will be impacted by the proposed chloride and mercury water quality standards. I will discuss the Lemont Refinery's options, which is only a fraction of the economic impact these proposed changes will have.

First, it is assumed that if the Board adopted the proposed chloride standard, the Agency would issue an NPDES permit that imposed a 500 mg/L chloride water quality limit ONLY when the Ship Canal is above 500 mg/L chlorides. Then the Lemont Refinery would have three options, one being to install reverse osmosis on the high chloride wastewater streams with a multi-effect evaporator on the reverse osmosis reject stream. The second option would be to hold the two streams that contribute chlorides; the crude unit desalter and the zeolite regeneration stream. The capital cost for pretreatment followed by reverse osmosis and evaporation of the reject stream from the reverse osmosis units for these two streams is estimated at \$42 million. The problem with both the first and second alternatives are that during periods when the Ship Canal is above 500 mg/L chlorides, no chlorides would allow to be added, so the Lemont Refinery would still not achieve the 500 mg/L effluent limit from other incidental sources.

The third alternative that would achieve compliance with a 500 mg/L chloride daily limit during periods when the Ship Canal is above 500 mg/L would be to literally store the entire effluent until there is sufficient assimilative capacity in the Ship Canal to discharge. We know from our monitoring that three weeks retention would be required. At 5.79 million gallons per day for 21 days, a holding capacity for 122 million gallons would be needed. There is no room for such a retention basin on the Refinery property, the closest area would be south of the Refinery, necessitating the construction of pump station and force main, plus the permitting of a new outfall. Assuming a 20 ft depth, the pond would occupy approximately 19 acres, plus road and fence. The constructed costs for such a basin would be on the order of \$21 million, and given the rock excavation, land purchase, and easements to secure take a minimum of five years to complete. This \$21 million would not remove any chlorides from the Ship Canal; it would only retard any contribution from the Lemont Refinery during periods the chlorides in the Ship Canal are above 500 mg/L.

Most of the mercury in the Lemont Refinery's effluent is present in particulate form. This is consistent with what other refineries have reported. The mercury particulates tend to be extremely fine in particle size. Phillips 66 pilot tested a granular media filtration system, and estimated that such a system could be installed for an estimated cost of \$18.5 million, excluding management of the backwash stream that would contain elevated mercury<sup>1</sup>. Management of this backwash stream is a significant engineering issue and cost. Argonne and Purdue University have been working on mercury technologies on behalf of the BP Whiting Refinery. These researchers have found mercury accumulating within the sand filters while adding a chemical agent to improve mercury removal. This accumulation is a concern because it is not known at this time whether the mercury will ultimately pass through the filter (at very high concentrations) when conditions change in the incoming water. Argonne/Purdue estimated a cost for a full-scale ultrafiltration system at between \$39 and \$147 million dollars for a 40 million gallon per day system. Similar to the Phillips 66 pilot work, these researchers have not

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<sup>1</sup> See PCB 12-101, Transcript at pages 40-41

worked out the treatment process for the reject stream from the ultrafiltration system or the backwash from the filters<sup>2</sup>.

For the Lemont Refinery to meet a 12 ng/L limit, remembering the influent averages 9.59 ng/L mercury, would necessitate treating the Design Average Flow (5.79 mgd), and bypassing higher flows. Extrapolating from the cost estimates of the Phillips 66 and BP estimates based simply on flow, yields a cost range from \$13 to \$47 million dollars. This expenditure would effectively reduce the net mercury contribution from the Lemont Refinery (Attachment 2) from 0.075 pounds per year to no net contribution.

Compounding both the chloride and mercury costs to all of the industrial dischargers and municipal dischargers yields a cost that Illinois can ill afford. Based on the mass balance for chlorides I presented earlier and the mercury data which suggests sediment re-suspension is the issue, even if these costs are invested, the Ship Canal would not achieve 500 mg/L chlorides in the winter months nor would it meet the 12 ng/L mercury proposed water quality standard when the flows are above the harmonic mean. Given USEPA's current position on variances, relief may be very difficult to secure. All of these factors suggest we need to find a better way to address mercury and chlorides. Logically that better way would be waiting for the TMDL studies to be completed before adopting standards that will result in the imposition of water quality based effluent limits that have not been demonstrated will result in achieving the proposed water quality standards.

The economic impact on the Lemont Refinery from these two proposed water quality changes is significant. This Refinery provides employment for 520 employees and an average of 400 contractors. Fifty two percent of its production is gasoline, sold nearly exclusively in the Midwest, with the Chicago Area its biggest market. The Chicago Area has seen the impact on gasoline prices when any of the four local refineries have been temporarily shut down for planned and unplanned work.

More significantly, these two constituents show the effect of trying to simply apply general use standards onto a water body, the Chicago Sanitary & Ship Canal, where there

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<sup>2</sup> Module 4- Pilot Scale Testing- Joint Executive Summary. Purdue-Argonne, March 2012

are significant upstream sources and upstream legacy sediment of the same pollutants. In the case of the Lemont Refinery, it has installed Best Available Treatment (BAT) for the pollutants regulated by USEPA and then spent tens of millions of dollars to meet the ammonia nitrogen rule adopted by the Board. In this proceeding, the only proposed standards to pose issues for most discharges are chlorides and the mercury standard to protect fish consumption that may occur further downstream. Both of these issues are clearly caused by upstream sources. The Lemont Refinery contributes less than 0.2% of the pollutant loading in the Ship Canal for these constituents.

**Suggested Alternative Regulatory Approach**

Mercury has been identified as a toxic compound, and as a society we have expended considerable efforts to reduce mercury discharges to the environment. Unfortunately, the legacy in sediment remains a concern that is not addressed through the NPDES process. Chlorides, as discussed above, cannot be effectively regulated through point source NPDES permit limits when de-icing practices is the problem. Roger Klocek has developed alternative winter chloride standards based on actual species present in the Ship Canal, similar to the Board specifically identifying fish species present in Use B waters. Mr. Klocek also included actual benthic and plankton organisms present. While adoption of Mr. Klocek's proposed winter limits would resolve the chloride issue on the Ship Canal, his approach will not help the General Use waterways in Illinois due to the presence of more sensitive species. The USEPA is actively researching the effects of chlorides on a number of sensitive species, with the likely outcome that USEPA will request a lowering its chronic chloride criterion of 230 mg/L in its next water quality evaluation. Urban streams don't achieve 500 mg/L chlorides, lowering a standard to 200 mg/L or lower will compound this problem, no matter what limits are imposed in NPDES Permits. However, these sensitive species are not present in the Ship Canal.

Until the TMDL on chlorides is completed and before numeric limits are adopted, I would recommend a *Best Management Practices* (BMP approach) for chlorides. This approach could be easily rolled into the existing storm water NPDES program. A goal could be to reduce chlorides discharged from point sources by the equivalent of the

chloride contribution over 500 mg/L, whenever the Ship Canal is over 500 mg/L. Such a program could remain in place until a TMDL study was completed and the adoption of numeric water quality standards. The net result would be that such a commitment would be essentially offsetting a discharger's contribution to water quality exceedences, and therefore would be eligible for a mixing zone for chlorides because it would no longer be causing or contributing to water quality exceedences.

The Lemont Refinery has spent considerable effort looking for opportunities to reduce its chloride contribution to the waterways to offset the 119 tons it contributes during periods when the Ship Canal is above 500 mg/L chlorides. The Refinery has over three million square feet of impervious surfaces that require snow removal. Like highway departments, the Lemont Refinery has historically relied upon rock salt to provide safe conditions for its employees and visitors. There are opportunities, through the same technologies available to highway departments, including anti-icing, pre-wetting, calibration, training, better weather data, and learning from each storm event to reduce its salt usage by over 119 tons per year as chlorides, or 196 tons as sodium chloride. The Lemont Refinery is proceeding with implementing these steps with the expectation it can more than offset the 119 tons per year of chlorides it contributes during the periods when the Ship Canal is above 500 mg/L. As with any new technologies and the concern over safety, it will take several winter seasons to achieve these goals and the BMPs will be adjusted as lessons are learned. The BMP plan, as currently contemplated, would measure chloride usage on a five-year running average so that variations in snow fall would be balanced out.

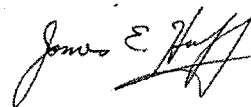
A similar approach could be taken for mercury. Until a TMDL is completed for mercury on the Use B waters to address how to achieve a Human Health Standard, a Special Condition could be added to NPDES permits requiring a *Best Management Practices* plan for identifying and reducing mercury released into the environment, not just into water. This would make the approach more holistic and would allow dischargers to focus where the maximum cost effective benefit to society could be achieved, and allow the Agency to begin to collect better data on mercury releases into the environment. One other suggestion is to only adopt the 12 ng/L water quality standard as an annual average basis. For the Use B waters, the imposition of the 12 ng/L during periods when the flow

is above the harmonic means makes no sense technically, and eliminating this portion of the proposed regulation would resolve the mercury issue, but for the whether a mixing zone can be applied to mercury in a Use B water. The condition to achieve the 12 ng/L mercury during higher flows periods cannot be achieved without dredging of the Ship Canal, and who bears those costs is a discussion for another day.

**Conclusion**

The Board has an opportunity to develop a non-traditional approach to water quality standards for chlorides and modify the Agency's mercury proposal for the Use B waters. If the Board adopts the Agency's proposed water quality standards for chlorides and mercury for the Use B waters, the result will be widespread hardships on all point source discharges that contribute either pollutant, with the Agency imposing the water quality standards as effluent limits. With USEPA's position on variances and site specific changes, economic hardship will result. The expenditures of hundreds of million dollars on point source control will not eliminate the chloride and mercury issues on the Use B waters, as the primary sources are being ignored. Until the TMDL studies are completed, a Best Management Practices approach is a better approach, and will lead to a greater improvement in water quality.

Thank you, this concludes my pre-filed testimony.



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James E. Huff, P.E.

ATTACHMENT I  
MERCURY LEVELS  
CHICAGO SANITARY & SHIP CANAL-LEMONT REFINERY INTAKE

	Dissolved Hg, ng/L	Dissolved Hg, 4-day Running average, ng/L	Total Hg, ng/L Human Health Std	Stream Flow, cfs
General Use WQ Stds	2200.00	1100.00	12.00	
07/24/08	<0.50		11.10	
07/31/08	<0.50		9.66	
08/06/08	0.64		<b>15.50</b>	<b>3,434</b>
08/11/08	<1.01	0.41	4.73	2,655
08/13/08	<0.50	0.41	13.00	2,255
08/18/08	0.50	0.47	9.48	
08/20/08	1.69	0.74	5.82	
08/25/08	<0.50	0.67	4.91	
08/27/08	<0.50	0.67	7.50	
09/03/08	<0.50	0.61	9.16	
02/22/11	<0.50		<b>23.80</b>	<b>7,400</b>
03/01/11	<0.50		5.92	4,700
03/08/11			5.66	3,410
03/15/11			3.44	1,290
03/22/11			10.40	2,050
03/29/11			2.92	489
04/05/11			2.17	875
04/12/11			5.30	1,220
04/19/11			<b>14.40</b>	<b>3,300</b>
04/26/11			<b>26.90</b>	<b>8,600</b>
<b>Average</b>			<b>9.59</b>	

Acute and Chronic based upon Critical hardness of 205 mg/L.

Chronic applies to four-day running average

Human Health Std based on annual average, total mercury, and shall also not be exceeded when the flow is above the harmonic mean.

The Harmonic mean flow for the Ship Canal is 2,900 cfs



ATTACHMENT 2  
CHICAGO SANITARY & SHIP CANAL CHLORIDE LEVELS AT ROMEOVILLE, ABOVE LEMONT REFINERY OUTFALL

Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L	Influent Chloride, Date	Influent Chloride, mg/L
1/10/05	835	1/2/06	330	1/1/07	174	1/7/08	662	1/2/09	342	1/1/10	344	01/03/11	369	01/01/13	132
1/12/05	492	1/6/06	320	1/5/07	156	1/11/08	272	1/5/09	297	1/4/10	350	01/07/11	391	01/03/13	139
1/13/05	580	1/9/06	314	1/8/07	113	1/18/08	270	1/9/09	270	1/6/10	301	01/10/11	291	01/08/13	156
1/14/05	274	1/13/06	276	1/12/07	133	1/21/08	256	1/12/09	300	1/8/10	276	01/14/11	286	01/10/13	161
1/17/05	242	1/16/06	226	1/15/07	250	1/25/08	252	1/16/09	436	1/11/10	223	01/17/11	407	01/15/13	63
1/19/05	250	1/20/06	215	1/19/07	239	1/28/08	514	1/19/09	470	1/15/10	311	01/21/11	264	01/17/13	154
1/21/05	235	1/23/06	220	1/22/07	203	2/1/08	556	1/23/09	331	1/18/10	267	01/24/11	521	01/22/13	156
1/24/05	430	1/27/06	413	1/26/07	384	2/4/08	625	1/26/09	262	1/22/10	297	01/28/11	277	01/24/13	164
1/31/05	634	1/30/06	308	1/29/07	286	2/8/08	896	1/30/09	224	1/25/10	342	01/31/11	348	01/29/13	156
2/4/05	413	2/3/06	298	2/2/07	225	2/11/08	848	2/2/09	298	1/29/10	281	02/04/11	353	01/31/13	280
2/11/05	416	2/6/06	252	2/5/07	227	2/15/08	666	2/6/09	214	2/1/10	310	02/07/11	365	02/05/13	207
2/14/05	364	2/10/06	243	2/9/07	181	2/18/08	489	2/9/09	270	2/5/10	259	02/11/11	425	02/07/13	284
2/25/05	307	2/13/06	238	2/12/07	224	2/22/08	351	2/13/09	402	2/8/10	305	02/14/11	605	02/12/13	569
3/7/05	283	2/17/06	251	2/16/07	181	2/25/08	376	2/16/09	355	2/12/10	283	02/18/11	1099	02/14/13	640
3/11/05	286	2/20/06	276	2/19/07	695	2/29/08	299	2/20/09	310	2/15/10	833	02/21/11	504	02/19/13	375
3/14/05	277	2/24/06	249	2/23/07	549	3/3/08	460	2/23/09	344	2/19/10	446	02/25/11	388	02/21/13	325
3/21/05	300	2/27/06	484	2/26/07	600	3/7/08	398	2/27/09	376	2/26/10	648	02/28/11	423	02/26/13	284
3/25/05	272	3/3/06	200	3/2/07	734	3/10/08	364	3/2/09	255	3/1/10	559	03/04/11	401	02/28/13	418
3/28/05	270	3/17/06	209	3/5/07	616	3/14/08	333	3/6/09	881	3/3/10	580	03/07/11	336	03/05/13	659
4/4/05	240	3/20/06	201	3/9/07	395	3/17/08	316	3/9/09	167	3/5/10	528	03/11/11	341	03/07/13	711
4/8/05	232	3/31/06	189	3/12/07	250	3/12/08	301	3/13/09	198	3/8/10	422	03/14/11	353	03/12/13	450
4/11/05	221	4/3/06	208	3/16/07	350	3/24/08	294	3/16/09	237	3/12/10	343	03/18/11	348	03/14/13	298
4/15/05	200	4/7/06	189	3/19/07	340	3/28/08	388	3/20/09	252	3/19/10	536	03/21/11	286	03/19/13	398
4/18/05	199	4/10/06	183	3/23/07	281	3/31/08	413	3/23/09	249	3/22/10	261	03/25/11	273	03/21/13	275
4/22/05	197	4/14/06	188	3/23/07	281	4/4/08	333	3/27/09	245	3/22/10	261	03/28/11	252	03/26/13	282
4/25/05	196	4/17/06	190	3/26/07	415	4/7/08	328	3/30/09	237	3/26/10	259	04/01/11	257	03/28/13	345
4/29/05	184	4/21/06	128	3/30/07	258	4/11/08	275	4/3/09	225	3/29/10	285	04/04/11	201		
		4/24/06	154	4/2/07	252	4/14/08	247	4/6/09	228	4/2/10	266	04/08/11	254		
		4/28/06	162	4/6/07	236	4/18/08	158	4/10/09	210	4/5/10	246	04/11/11	218		
				4/9/07	232	4/21/08	266	4/13/09	231	4/9/10	187	04/15/11	221		
				4/13/07	214	4/25/08	251	4/17/09	214	4/12/10	192	04/18/11	237		
				4/16/07	242	4/28/08	242	4/20/09	240	4/16/10	210	04/22/11	188		
				4/20/07	259			4/24/09	218	4/19/10	215	04/25/11	164		
				4/23/07	241			4/27/09	220	4/23/10	218	04/29/11	155		
				4/27/07	136					4/28/10	191				
				4/27/07	136					4/30/10	197				
				4/30/07	169										
11/4/05	146	11/3/06	134	11/2/07	111	11/3/08	145	11/2/09	72	11/1/10	104				
11/7/05	126	11/6/06	149	11/5/07	122	11/7/08	146	11/6/09	111	11/5/10	107				
11/11/05	105	11/13/06	118	11/9/07	120	11/10/08	152	11/9/09	158	11/8/10	684				
11/14/05	132	11/17/06	108	11/12/07	127	11/14/08	115	11/11/09	134	11/12/10	121				
11/18/05	110	11/20/06	128	11/16/07	130	11/17/08	147	11/13/09	137	11/15/10	870				
11/21/05	116	11/24/06	140	11/19/07	128	11/21/08	149	11/16/09	151	11/19/10	123				
11/25/05	128	11/27/06	143	11/23/07	122	11/24/08	154	11/20/09	137	11/22/10	142				
11/28/05	128	12/1/06	105	11/26/07	100	11/28/08	149	11/23/09	133	11/26/10	111				
12/2/05	146	12/4/06	14	11/30/07	103	12/1/08	155	11/27/09	145	11/29/10	87				
12/5/05	130	12/8/06	195	12/7/07	261	12/5/08	133	11/30/09	119	12/3/10	91	12/04/12	121		
12/9/05	183	12/11/06	236	12/10/07	717	12/8/08	244	12/4/09	119	12/6/10	111				
12/12/05	192	12/15/06	249	12/14/07	654	12/12/08	272	12/7/09	143	12/10/10	295	12/06/12	139		
12/16/05	406	12/18/06	200	12/17/07	404	12/15/08	277	12/9/09	144	12/13/10	177	12/11/12	130		
12/19/05	264	12/22/06	198	12/21/07	998	12/19/08	313	12/11/09	286	12/17/10	316	12/13/12	145		
12/23/05	295	12/25/06	129	12/24/07	614	12/22/08	337	12/14/09	275	12/20/10	316	12/18/12	124		
12/26/05	253	12/29/06	139	12/28/07	488	12/26/08	448	12/18/09	301	12/24/10	259	12/20/12	133		
12/30/05	357			12/31/07	412	12/29/08	385	12/21/09	259	12/27/10	326	12/24/12	116		
								12/25/09	412	12/31/10	525	12/27/12	115		
								12/28/09	424						
<b>Average</b>	<b>274</b>	<b>211</b>	<b>305</b>	<b>333</b>	<b>258</b>	<b>311</b>	<b>347</b>	<b>128</b>	<b>311</b>	<b>1099</b>	<b>145</b>	<b>311</b>	<b>711</b>		
<b>Maximum</b>	<b>835</b>	<b>484</b>	<b>998</b>	<b>896</b>	<b>881</b>	<b>870</b>	<b>1099</b>	<b>145</b>	<b>870</b>	<b>1099</b>	<b>145</b>	<b>1099</b>	<b>145</b>		

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# The Sources, Distribution, and Trends of Chloride in the Waters of Illinois

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March 2012

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Champaign, Illinois



**The Sources, Distribution, and Trends of Chloride in the Waters of Illinois**

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### **Abstract**

Chloride ( $\text{Cl}^-$ ) is a major anion found in all natural waters. It occurs naturally and is also a relatively minor contaminant. Chloride concentrations in Illinois range from less than 0.1 milligrams per liter (mg/L) in precipitation to close to 100,000 mg/L in Paleozoic brines. Chloride is non-toxic to humans, although there is a secondary drinking water standard of 250 mg/L. It is, however, deleterious to some plants and aquatic biota, thus the Illinois Environmental Protection Agency (IEPA) has set an acute standard of 500 mg/L for surface waters in Illinois. Chloride is also a very corrosive agent, and elevated levels pose a threat to infrastructure, such as road beds, bridges, and industrial pipes.

Some streams and aquifers in Illinois have naturally elevated  $\text{Cl}^-$  concentrations due to surface or near-surface discharge of Paleozoic brines. Of greater concern to water resources in Illinois are anthropogenic sources of  $\text{Cl}^-$ , including road salt runoff, sewage, water conditioning salts, and fertilizer. Chloride concentrations are elevated in most water bodies in the Chicago region, primarily due to road salt runoff. Concentrations have been increasing since approximately the 1960s, and in general, concentrations continue to increase. These elevated  $\text{Cl}^-$  concentrations may pose a risk to infrastructure as well as aquatic to ecosystems.

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## Introduction

Chloride ( $\text{Cl}^-$ ) is a naturally occurring major anion found in all natural waters. Chloride behaves as a conservative ion in most aqueous environments, meaning its movement is not retarded by the interaction of water with soils, sediments, and rocks. As such, it can be used as an indicator of other types of contamination. Anomalously high concentrations can act as an "advance warning" of the presence of other more toxic contaminants. Concentrations of  $\text{Cl}^-$  in natural waters can range from less than 1 milligram per liter (mg/L) in rainfall and some freshwater aquifers to greater than 100,000 mg/L for very old groundwaters within deep intracratonic basins (Graf et al., 1966; Psenner, 1989). Its concentration in precipitation in mid-continental regions (far from oceans and other salt sources) is almost always less than 1 mg/L, and often less than 0.1 mg/L (NADP, 2011). Upon contacting land surface,  $\text{Cl}^-$  concentrations in water increase as a result of interaction with soils, rocks, and biota (waste products), as well as the effects of evaporation. Chloride is the most abundant ion in seawater, with a concentration greater than 19,000 mg/L (Stumm and Morgan, 1996). Extremely elevated levels of  $\text{Cl}^-$  in surface water are generally due to significant evaporation (e.g., the Dead Sea has a  $\text{Cl}^-$  concentration  $> 230,000$  mg/L).

Chloride is non-toxic to humans, but elevated levels make water unpotable due to the salty taste. In the U.S., there is a secondary (non-enforced) drinking water standard of 250 mg/L, but in areas of the world with water scarcities, drinking water can have considerably greater concentrations of  $\text{Cl}^-$ . Chloride is corrosive to steel, thus it may corrode pipes in water treatment and industrial plants. Because it imparts a salty taste to water and is corrosive, elevated  $\text{Cl}^-$  levels in drinking water supplies can lead to increased treatment costs. Elevated  $\text{Cl}^-$  in surface water has been linked to damage of terrestrial and aquatic plants and aquatic animals at concentrations as low as 210 mg/L (Environment Canada, 2001; Hart et al., 1991; Kaushal et al., 2005; Wilcox, 1986). The U.S. Environmental Protection Agency (USEPA) recommends a chronic criterion for aquatic life of a four-day average  $\text{Cl}^-$  concentration of 230 mg/L with an occurrence interval of once every three years (USEPA, 1988). The recommended acute criterion is 860 mg/L, which relates to a one-hour average concentration with a recurrence interval of less than once every three years. The Illinois EPA (IEPA) uses an acute criterion of 500 mg/L, but there is no chronic standard. The government of British Columbia has proposed a lower maximum  $\text{Cl}^-$  concentration of 600 mg/L and a 30-day average concentration of 150 mg/L to protect freshwater life (Nagpal et al., 2003). Increased  $\text{Cl}^-$  concentrations in some environments have killed off native vegetation and allowed invasive salt-tolerant species to thrive (Panno et al., 1999).

The objective of this report is to characterize the sources, distribution, and trends of  $\text{Cl}^-$  in the waters of Illinois, including rainwater, lakes, rivers and streams, groundwater, and wetlands.

### **Acknowledgements**

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### **Natural Sources of Chloride**

#### **Precipitation**

Chloride in precipitation and dry deposition originates from marine aerosols or volcanic gases. Naturally-occurring Cl<sup>-</sup> concentrations in rainwater and snowmelt can be several mg/L near the coastal regions of the U.S. due to the contribution of seawater aerosols (Figure 1). Chloride concentrations in mid-continental regions are much lower. Concentrations in Illinois are typically less than 0.1 mg/L (NADP, 2011).

Saline groundwater in Illinois is under pressure, and at many locations it discharges into shallower aquifers or at the land surface as saline springs (Bartow et al., 1909; Willman et al., 1975; Cartwright, 1970; Panno et al., 1994, 2006). Bedrock discharge into the Mahomet Aquifer in Piatt County in east-central Illinois increases the Cl<sup>-</sup> concentration from less than 10 mg/L to concentrations as high as 500 mg/L (Hackley et al., 2010). Thirteen samples of brine-affected groundwater collected by Panno et al. (2006), primarily in the southern part of the state, had a median Cl<sup>-</sup> concentration of 474 mg/L. In some parts of Illinois, especially in the south, these deep brines discharge to surface waters, increasing the natural Cl<sup>-</sup> concentration. For example, the North Fork of the Saline River in southeastern Illinois, named for its natural saltiness, had a median Cl<sup>-</sup> concentration of 109 mg/L between 1978 and 1997 (USGS, 2009).

### Background Chloride Concentrations

Despite the existence of saline seeps in Illinois, the vast majority of groundwater has relatively low concentrations of Cl<sup>-</sup>, especially in major aquifers. In a study of shallow groundwater (< 100 meters) in northern Illinois, Panno et al. (2006) determined that Cl<sup>-</sup> concentrations in shallow aquifers ranged from less than 1 to 15 mg/L. They suggested that concentrations greater than 15 mg/L indicated contamination from human sources. This threshold is probably similar (or lower) for aquifers in the rest of Illinois as well, where urbanization is less (Panno et al., 2005). Prior to human alterations to the landscape, almost all water discharging to surface streams in Illinois passed through the subsurface (i.e., groundwater), and a large majority still does. Thus pristine surface waters in Illinois should have Cl<sup>-</sup> concentrations < 15 mg/L. Lusk Creek, for example, which flows through the undeveloped Shawnee National Forest in southern Illinois, had a median Cl<sup>-</sup> concentration of 2.3 mg/L between 1978 and 1997 (USGS, 2009).

### Anthropogenic Sources

Schlesinger (2004) estimated that more than 140 teragrams (140 trillion kilograms) of Cl<sup>-</sup> are annually cycled through various reservoirs on Earth, almost all of it due to human activities. Anthropogenic sources include human sewage, livestock waste, water conditioning salt, synthetic fertilizer (primarily KCl), brine disposal pits associated with oil fields, chemical and other industries, and, in snowy climates, road salt runoff. From a volume standpoint, the most important anthropogenic sources of Cl<sup>-</sup> to waters in Illinois are fertilizer, road salt, water conditioning salt, sewage, and livestock waste (Table 1). Chloride concentrations for potential contamination sources of Cl<sup>-</sup> in Illinois are shown in Table 2. Once in groundwater, Cl<sup>-</sup> and other contaminants can persist for many years if travel times are slow. For example, Howard et al. (1993) estimated that if road salting was stopped immediately in the Toronto area, it would be decades before the Cl<sup>-</sup> concentrations returned to pre-1960 levels in shallow groundwater. In rural areas, agricultural sources of Cl<sup>-</sup> are of greater importance. Oil field-related contamination problems have occurred primarily in the southern two-thirds of Illinois.



**Table 1. Annual Chloride Fluxes in Illinois**

<i>Source</i>	<i>Flux (metric tons)</i>
Treated Wastewater	
MWRDGC	175,000
Remainder of state	125,000
Atmospheric	18,000
Road Salt	471,000
Water Conditioning Salt	135,000
Fertilizer (KCl)	373,000
Livestock	139,000
Lake Michigan withdrawals	34,000
Groundwater withdrawals	
Public supply wells	12,500
Industrial/commercial	5,300
Irrigation	10,000
Oil-Field Brines	23,000

Note: The treated wastewater fluxes do not include road salt inputs.

**Table 2. Chloride Concentrations (mg/L) for Potential Sources in Illinois**

<i>Sample Type</i>	<i>Location</i>	<i>Min</i>	<i>Median</i>	<i>Max</i>	<i>Reference</i>
Tile Drain	Ludlow	10.3	14.5	17.8	Kelly et al. (2010)
	Champaign	23.1	25.4	36.5	Panno et al. (2005)
Treated Wastewater	Stickney (2000-2008)	26.3	145	1,481	MWRDGC
Road Salt Runoff	Willow Springs		8,930		Kelly et al. (2010)
	Pekin		1,572		Kelly et al. (2010)
Agricultural Soil Water	Central Illinois	16.2	17.5	20.8	W. Kelly (unpublished data)
Natural Brine	Central Illinois		6,517		Panno et al. (2006)
	SW Illinois		8,080		Panno et al. (2006)
Illinois Basin Brine		557	64,600	125,000	Panno et al. (2006)
Livestock Manure	Central Illinois	440	847	1,980	Panno et al. (2006)
Septic System Discharge	SW Illinois	20.8	91	5,620	Panno et al. (septic paper)
Landfill Leachate		198	1,284	6,170	Panno et al. (2006)

### Human Waste

The median  $\text{Cl}^-$  concentration in treated wastewater (TWW) discharging from the Stickney wastewater treatment plant (WWTP) in Chicago (the largest in the U.S.) between 2000 and 2008 was 145 mg/L (based on weekly sampling) (MWRDGC, 2010) (Table 2). Kelly et al. (2010) got similar results in samples collected on three dates between 2003 and 2005 from two Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) WWTPs (Stickney and Calumet); they reported a median  $\text{Cl}^-$  concentration of 141 mg/L. Kelly et al. (2010) also collected samples from the Peoria WWTP, which had  $\text{Cl}^-$  concentrations that ranged from 113 to 291 mg/L. TWW is generally discharged directly into surface waterways in Illinois.

### Livestock Waste

Animal waste contains elevated concentrations of  $\text{Cl}^-$ ; Panno et al. (2006) measured levels as high as 1980 mg/L (Table 2). Because of this, even relatively small concentrations of livestock can create a local problem for shallow groundwater. Large confined animal feeding operations, which can concentrate thousands of animals in a relatively small area, have the potential to produce more widespread contamination of shallow groundwater, streams, and rivers (Wing et al., 2002; Showers et al., 2008).

### Road Deicers

The chemical industry and governmental departments handling road ice control are the major importers and consumers of halite in the U.S., accounting for about three-fourths of its total use (Kostick, 2008). Road salt has been linked to groundwater degradation in many urban and roadside areas in snowy climates (Amrhein et al., 1992; Bester et al., 2006; Howard and Haynes, 1993; Huling and Hollocher, 1972; Pilon and Howard, 1987; Williams et al., 2000b). Significant application of road salt began after World War II and accelerated rapidly from the 1960s (Figure 3) (Salt Institute, 2009). Chloride concentrations have been increasing in surface waters and groundwater in urban regions of the northern United States and Canada since the 1960s, primarily due to road salt runoff (Godwin et al., 2003; Howard and Haynes, 1993; Kaushal et al., 2005; Kelly, 2008; Novotny et al., 2009; Kelly et al., 2010).

Two road salt runoff samples collected by Kelly et al. (2010) dripping off road bridges in Pekin and Willow Springs, IL, had very high concentrations of  $\text{Cl}^-$ : 1572 and 8930 mg/L, respectively (Table 2). Chloride concentrations in road salt runoff samples are extremely variable due to variability in application rates, snowfall amounts, melting rates, etc.; the values measured by Kelly et al. (2010) fall within the range of values reported by others (Amrhein et al., 1992; Environment Canada, 2001; Greb et al., 2000; Pilon and Howard, 1987). Road salt also can increase  $\text{Cl}^-$  concentrations in precipitation. For example, Williams et al. (2000a) characterized road salt aerosol in suburban areas west and south of Chicago, and measured  $\text{Cl}^-$  concentrations up to 9.4 mg/L in samples collected after snow events. They also found that  $\text{Cl}^-$  concentrations in snow samples decreased exponentially with distance from major highways.

Road salt runoff that recharges the soil zone and shallow groundwater can produce very high concentrations of  $\text{Cl}^-$ . Kelly and Roadcap (1994) measured  $\text{Cl}^-$  concentrations in excess of 1,000 mg/L in several shallow (< 25 ft; 7.6 m) monitoring wells installed along the uncurbed Interstate 94 in south Chicago, including two exceeding 3,500 mg/L.

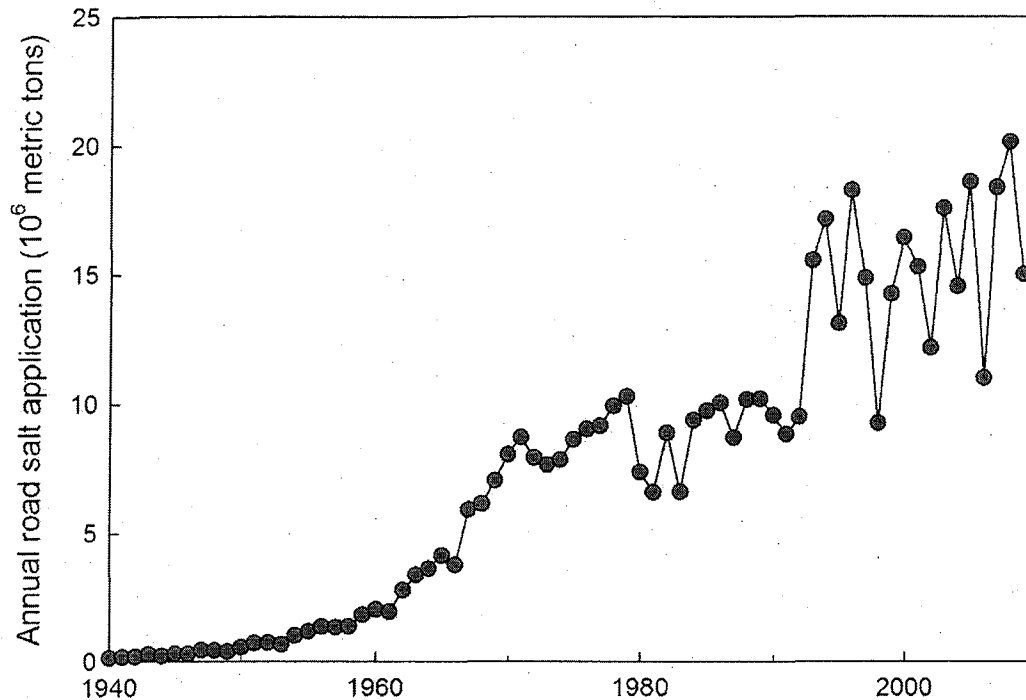


Figure 3. Yearly U.S. highway salt sales. Data from Salt Institute, 2011.

### Water Conditioning Salts

In-home water treatment, specifically water softening, typically uses NaCl to recharge ion exchange columns in order to reduce hardness (Ca + Mg) by replacement with Na. For a family of three or four with moderately hard water, the recommended amount of NaCl for water softening is between 1.8 and 2.7 kilograms per day, or 600 to nearly 1000 kg of NaCl per year (Panno et al., 2005, 2007). If a household uses on-site wastewater treatment, the Cl<sup>-</sup> is discharged to the shallow groundwater system via the leach field. If the household is connected to a community waste treatment facility, the Cl<sup>-</sup> (which is not removed in the treatment process) is generally discharged to streams or rivers.

### KCl Fertilizer

Illinois is a major producer of row crops, primarily corn and soybeans. KCl is the most commonly available potassium (K) fertilizer and usually the cheapest, thus it is widely applied in Illinois. Because it is spread over large areas (i.e., non-point source), its impact on soil water and

groundwater quality is less than more concentrated  $\text{Cl}^-$  applications, such as road salt. In much of Illinois, agricultural fields are tiled to facilitate drainage of soils, and these drain tiles are the major source of water to many streams in Illinois. Panno et al. (2005) and Kelly et al. (2010) collected samples from several tile drains in east-central Illinois, which represent shallow groundwater beneath row crop areas. Chloride concentrations in these tile drain samples ranged from 10 to 37 mg/L (Table 2). This is also approximately the same concentration range found in soil water in agricultural fields in central Illinois (W. Kelly, unpublished data).

#### Municipal Landfills

Panno et al. (2006) measured  $\text{Cl}^-$  concentrations in municipal landfill leachate as high as 6,170 mg/L. Roy (1994) reported the greatest  $\text{Cl}^-$  concentration recorded in municipal landfill leachate to be 27,100 mg/L. Potential sources of  $\text{Cl}^-$  in landfills include food scraps and pet wastes. Chloride concentrations in landfills are not static, but decrease with the age of the landfill (McGinley and Kmet, 1984; Ham, 1980; Lu et al., 1985). Farquhar (1989) reported that  $\text{Cl}^-$  concentrations in municipal landfill leachate tend to decrease asymptotically with time, with concentrations 1,000–3,000 mg/L during the first five years, 500–2,000 mg/L during years 5 to 10, 100–500 mg/L during years 10 to 20, and < 100 mg/L after that.

#### Oil and Gas Exploitation

Leakage of brine-holding ponds associated with oil wells has locally contaminated groundwater with high TDS waters in southeastern Illinois. Hensel and McKenna (1989) installed shallow monitoring wells around two brine-holding ponds in Clay County and measured  $\text{Cl}^-$  concentrations over 10,000 mg/L in several samples. They identified 384 holding ponds in their study area (~300  $\text{mi}^2$  in southeastern Clay County), so the potential for widespread groundwater contamination is significant and hundreds of acres of farm land were reported to have been made unsuitable for crops due to brine leakage and spillage. However, Hensel and McKenna (1989) found no widespread degradation of groundwater resources in the area.

#### Identification of Sources of Chloride

There are various methods for determining the source(s) of  $\text{Cl}^-$  in individual water samples, one of the best being halide ratios. In a recent investigation, Panno et al. (2006) collected more than 100 samples from various  $\text{Cl}^-$  sources (primarily in Illinois) and, by plotting  $\text{Cl}^-$  and bromide ( $\text{Br}^-$ ) data on a  $\text{Cl}^-$  vs.  $\text{Cl}^-/\text{Br}^-$  diagram, were able to define domains that distinguish among the sources (Figure 4). TWW can plot outside the septic effluent source domain because there are often multiple sources of  $\text{Cl}^-$  in TWW. Chicago and many of its suburbs have combined sewers (sewage and storm water), and an average of about 30 percent of the water entering the Stickney WWTP is from storm runoff (J. Wasik, MWRDGC, December 1, 2006, personal communication). The highest  $\text{Cl}^-/\text{Br}^-$  ratios in TWW measured by Kelly et al. (2010) were during the winter, which was due to a dominant road salt component.

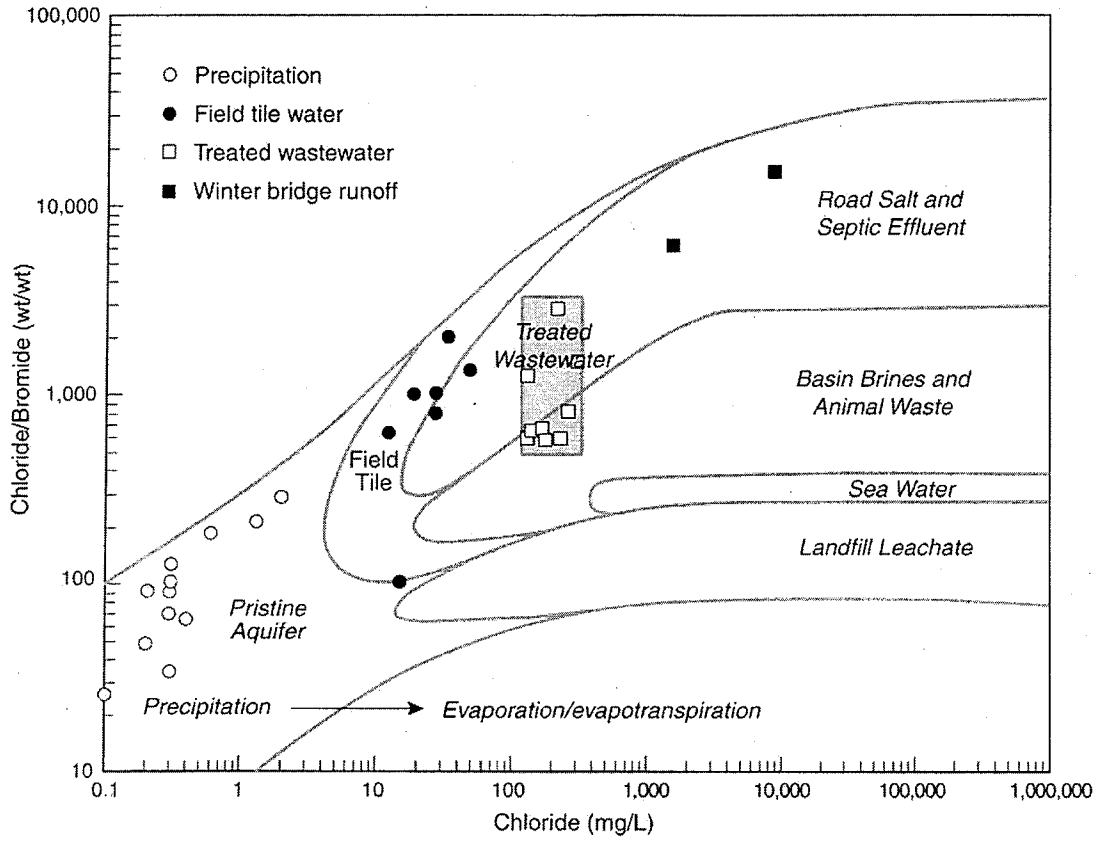


Figure 4. Cl/Br vs. Cl<sup>-</sup> plot showing source domains (Kelly et al., 2010)

### Annual Fluxes of Chloride in Illinois

The estimated annual flux of  $\text{Cl}^-$  in Illinois from various sources was determined using the methods of Kelly et al. (2010) (Table 2). They found that  $\text{Cl}^-$  in the Illinois River Basin was predominantly from road salt, TWW, and  $\text{KCl}$  fertilizer. An accurate estimate of how much road salt is applied in an average winter is difficult, due to the large number of government agencies and private entities that apply salt to roads and parking lots. Friederici (2004) and Keseley (2006) reported more than 250,000 metric tons of road salt is applied annually in the Chicago metropolitan region, but this is almost certainly an underestimate. Probably the best method for estimating road salt applications is to use road salt sales reported by the Salt Institute (Salt Institute, 2009) as a proxy. Using additional state data from Richter and Kreitler (1993) and Panno et al. (2005), Kelly et al. (2010) estimated that an annual average of 471,000 metric tons of road salt (equivalent to ~283,000 metric tons of  $\text{Cl}^-$ ) were used in Illinois for the years 2002 to 2005, mostly in the Chicago region. Average annual road salt sales have increased since 2005, so the amount of road salt applied in Illinois has undoubtedly increased as well. The amount applied in a particular year generally depends on how much snow and ice fall during winter.

The  $\text{Cl}^-$  flux for TWW from the Chicago region can be calculated from WWTP discharge and  $\text{Cl}^-$  concentration data reported by MWRDGC (MWRDGC, 2010), but this calculation is complicated by multiple sources in TWW and the potential for "double counting" of sources. In addition to human waste, TWW includes industrial effluent, water conditioning salt, and road salt, as well as  $\text{Cl}^-$  present in drinking water sources.

Chloride fluxes from the Chicago WWTPs were calculated using Cohn's equation (Kelly et al., 2010). Road salt contributions were removed from the WWTP loads by assuming that there was no road salt in TWW from May to October. Chloride loads during these months were divided by monthly discharges, and it was assumed that the same load per discharge ratio for non-road salt sources occurred between November and April. The remaining chloride loads between November and April (which varied between 17 percent and 50 percent of the total monthly load) were assumed to come from road salt and were removed from the TWW load calculations.

The seven MWRDGC plants account for almost 60 percent of the TWW discharged to surface water bodies in Illinois. To calculate the  $\text{Cl}^-$  flux for the remaining TWW, it was assumed that the effluent  $\text{Cl}^-$  concentration was the same as for the MWRDGC plants, resulting in a flux of 125,000 metric tons.

Human waste actually accounts for a small percentage of  $\text{Cl}^-$  in TWW. Adult humans excrete between 110 and 250 millimoles of  $\text{Cl}^-$  per day (3,900–8,860 mg day) (WebMD, 2011). Assuming 5,500 mg of  $\text{Cl}^-$  per day, a typical value for urine production (1.25 L/day), and a 2010 population of 12.83 million, results in about 32,000 metric tons of  $\text{Cl}^-$  from human urine annually in Illinois. Another approach taken by Mullaney et al. (2009) is to use per capita salt consumption based on the recommended daily adult sodium intake of 2,300 mg/d, which would include about 3,547 mg of  $\text{Cl}^-$ . A person on this diet would consume, and release, about 1.3 kg of  $\text{Cl}^-$  per year, which would be released by wastewater discharge. This would produce almost 17,000 metric tons of  $\text{Cl}^-$  in Illinois per year. Either estimate represents less than 10 percent of the  $\text{Cl}^-$  in TWW.

Chloride from water conditioning salt was also estimated from salt sales data. Between 2005 and 2008, approximately 3.2 million metric tons of salt (predominantly NaCl) was sold for water conditioning in the U.S. (Salt Institute, 2009). Assuming that water conditioning salt use was distributed equally across the U.S. based on population, approximately 135,000 metric tons of Cl<sup>-</sup> is annually consumed in Illinois by water conditioning.

About 80 percent of corn fields and 30 percent of soybean fields in Illinois receive potassium chloride (KCl) annually (USDA, 2008). The amount of KCl applied in Illinois was estimated from state fertilizer sales data (USDA, 2008). Between 2005 and 2007, an average of 373,000 metric tons of Cl<sup>-</sup> from KCl were purchased per year in Illinois.

Between 2005 and 2008, there were approximately 4.23 million pigs and 1.28 million cattle in Illinois (Illinois Agricultural Statistics Service, 2009). A pig produces about 3 gallons of waste a day and a cow produces 14 gal/day. Using Cl<sup>-</sup> concentrations of 3,680 mg/L and 3,000 mg/L for pigs and cows, respectively (DeRouchey et al., 2003; Lengemann et al., 1952), an annual total of 139,000 metric tons of Cl<sup>-</sup> was calculated to come from livestock.

For Cl<sup>-</sup> from precipitation, a Cl<sup>-</sup> concentration of 0.12 mg/L and an average annual precipitation of 102 centimeters (cm) were assumed (NAPD, 2011). This gives approximately 18,000 metric tons of Cl<sup>-</sup>.

One source of Cl<sup>-</sup> that may be overlooked is water extracted from Lake Michigan and groundwater for drinking, industrial, and agricultural purposes. Chicago and many of the inner suburbs obtain drinking water from Lake Michigan, which has a Cl<sup>-</sup> concentration of approximately 12 mg/L. Because most of the water Illinois takes from Lake Michigan is discharged outside the Great Lakes Basin, Illinois is limited by U.S. Supreme Court decree to 3,200 cubic feet per second (cfs) (~2,900 billion L/yr) of water from the lake. Assuming Illinois diverts all of this each year, approximately 34,000 metric tons of Cl<sup>-</sup> is removed from the lake. Most of this eventually finds its way into wastewater, which would be included in the TWW Cl<sup>-</sup> flux, and eventually is discharged down the Illinois River.

Approximately 1,180 million gallons (4,470 million L) of groundwater are withdrawn daily in Illinois (Kenny et al., 2009). About 507 million gallons per day (mgd) (1,920 million L/day) are used for drinking and other household uses, 517 mgd for agriculture (irrigation and livestock), 128 mgd by industrial and commercial applications, 15.5 mgd by mining, and 7.2 mgd for thermoelectric. Most extracted groundwater is not returned to the ground, but eventually finds its way to surface waters. In communities with sewers, most drinking water eventually finds its way into wastewater, which is then discharged to surface streams and rivers, eventually leaving the state. For homes and businesses with private wells and on-site sewage treatment (i.e., septic systems), extracted groundwater is discharged at or just below the ground surface, and most does not recharge underlying aquifers but is either evapotranspired or discharged to nearby streams or other surface waters. The same is true for irrigation water.

Groundwater withdrawal data are available for many public water supply wells and industrial/commercial wells. Of the top 200 pumped public water supply wells, 176 have been sampled sometime in the past 20 years, and the Cl<sup>-</sup> concentration and withdrawal data from 2008 were used to calculate the mass of Cl<sup>-</sup> removed. In order to not include potential surface contamination sources in shallow wells, it was assumed that the background Cl<sup>-</sup> concentration was 15 mg/L in all wells ≤ 250 feet deep. These results were then used to estimate Cl<sup>-</sup> fluxes

from the other approximately 2,500 public water supply wells for which we have withdrawal data. It was estimated that approximately 12,500 metric tons of  $\text{Cl}^-$  was extracted from public supply wells.

Sample results were available only for 13 of the top 200 industrial/commercial wells. For 184 of the other 187 wells, samples from a well located near to and at a similar depth to the well in question were found, and the  $\text{Cl}^-$  concentration from that well was used to calculate  $\text{Cl}^-$  fluxes. Using these data and the assumption that the background  $\text{Cl}^-$  concentration was 15 mg/L in all wells  $\leq$  250 feet deep gives an estimate of approximately 5,300 metric tons of  $\text{Cl}^-$  extracted annually from industrial/commercial wells.

In 2005, the U.S. Geological Survey estimated that approximately 479 million gallons of water were pumped from irrigation wells in Illinois (USGS, 2009). Withdrawal data from individual irrigation wells are lacking in Illinois. Because most irrigation wells are finished in relatively shallow sand and gravel aquifers, it was assumed that the  $\text{Cl}^-$  concentration was 15 mg/L. This gives a  $\text{Cl}^-$  flux of approximately 10,000 metric tons from irrigation wells.

It is difficult to get accurate estimates of how much water is withdrawn for oil and gas production. The most recent and most reliable estimates are from the 1980s, when Kirk (1987) reported that 25.5 million gallons per day (~9.3 billion gallons annually) were withdrawn. Almost all of this is reinjected for secondary oil and gas recovery. However, some of this brine was temporarily stored in ponds at the surface, and leakage to surface and shallow subsurface environments has been reported (Hensel and McKenna, 1989). Using the median concentration of 64,600 mg/L reported by Panno et al. (2006), and assuming leakage of 1 percent of the withdrawn brine, gives an annual  $\text{Cl}^-$  flux of approximately 23,000 metric tons.

### **Distribution and Trends in Chloride Concentrations in Waters of Illinois**

Recent research has suggested that  $\text{Cl}^-$  concentrations in many water bodies in Illinois are changing (e.g., Kelly [2008] and Kelly et al. [in press]), thus any report on the distribution of  $\text{Cl}^-$  is a "snapshot in time," subject to change. This is especially true for rivers and shallow groundwater in urban and urbanizing areas, most notably the Chicago region. In order to fully understand the distribution of  $\text{Cl}^-$  in the waters of Illinois, a discussion of temporal trends must also be included. Trends in  $\text{Cl}^-$  concentrations in surface water and groundwater can reveal much about the origin, evolution, character, and movement of its sources. Such information is critical to predicting future changes in  $\text{Cl}^-$  concentrations.

#### **Lakes**

As mentioned previously, Lake Michigan currently has an average  $\text{Cl}^-$  concentration of 12 mg/L, its highest historical level. Concentrations have been slowly increasing since the late 1800s, due to human inputs to the lake (Chapra et al., 2009), with an increase of about 3 mg/L since the 1980s (USEPA, 2011a) (Figure 5). While the increase seems small, it represents an additional annual load of approximately 600,000 metric tons of  $\text{Cl}^-$  to Lake Michigan.

Natural lakes in Illinois are primarily found in the northern part of the state, especially Lake and McHenry Counties. Most lakes in downstate Illinois are reservoirs created by the



## Rivers and Streams

Water quality data for streams and rivers in Illinois are available from several agencies, including the ISWS, USGS, MWRDGC, and IEPA. Chloride concentrations in streams in Illinois are highest in the Chicago region and lowest in streams in forested watersheds in far southern Illinois. The USGS has historical data from a number of streams and rivers throughout Illinois. A comparison of data sets from a time period with the greatest overlap of data (1990–1992) indicates that downstate rivers draining primarily agricultural watersheds (Kankakee, Spoon, La Moine) had median  $\text{Cl}^-$  concentrations  $< 30 \text{ mg/L}$  (Table 3 and Figure 8). Even though the North Fork of the Saline River drains an agricultural watershed, it has natural sources of  $\text{Cl}^-$  (geological brine discharge) and thus had a significantly higher median  $\text{Cl}^-$  concentration ( $86 \text{ mg/L}$ ). The Sangamon River, which has several large cities in its watershed (Bloomington-Normal, Decatur, Springfield), had a median concentration ( $34 \text{ mg/L}$  at its most downstream station, Oakford) higher than rivers draining primarily agricultural land. The Fox River, which drains some of the western suburbs of the Chicago region and receives TWW, had an even higher median concentration ( $70 \text{ mg/L}$  at its most downstream station, Dayton). Major Chicago waterways, including the Des Plaines River and the Chicago Sanitary & Ship Canal (CSSC), had median values  $> 90 \text{ mg/L}$ . The median  $\text{Cl}^-$  concentration in the Illinois River, which receives water from tributaries in the Chicago region as well as down-state, is  $> 60 \text{ mg/L}$  at Peoria and upstream, dropping to around  $50 \text{ mg/L}$  near its discharge to the Mississippi. Figure 9 shows that there are large annual variations in  $\text{Cl}^-$  concentrations in rivers throughout Illinois.

The MWRDGC has been monitoring water quality monthly at surface water stations in the Chicago region since 1975, primarily in Cook County but also at a few stations in DuPage and Will Counties (Figure 10). Forty-one stations have been monitored relatively continuously since 1975, with more than 30 others having a shorter period of record. Median  $\text{Cl}^-$  concentrations in 2008 were  $> 150 \text{ mg/L}$  at about 80 percent of the stations (Figure 11 and Table 4). The highest values tended to be in the smallest streams in northern Cook County, including Higgins Creek, Salt Creek, and Buffalo Creek, as well as the North Branch of the Chicago River. The stream with the lowest values appears to be the North Shore Channel, which receives significant flow from Lake Michigan.

The presence of trends in  $\text{Cl}^-$  concentrations were determined using Kendall's tau test at the 95 percent confidence level, and annual rates of change were estimated by calculating slope coefficients ( $\beta_1$ ) on 5-point running medians (Helsel and Hirsch, 2002). Rivers draining the Chicago region, including the Illinois River, have increasing trends in  $\text{Cl}^-$  concentrations. Of the 41 stations monitored by MWRDGC since 1975, 35 had statistically significant positive trends in  $\text{Cl}^-$  concentrations, with a median increase of  $2.7 \text{ mg/L}$  per year (Table 5). Five stations had increases of greater than  $5 \text{ mg/L/yr}$ ; two of these stations were in the North Branch of the Chicago River. Of a total of 78 USGS stations tested throughout the entire state, 36 had significant positive trends in  $\text{Cl}^-$  concentrations, and 10 had significant negative trends (Table 6). The positive stations included almost all the Chicago region rivers and canals (Des Plaines River, Fox River, Chicago River, Addison Creek, CSSC), as well as a number of down-state rivers, including the Kankakee, Rock, and Sangamon Rivers. All of the Illinois River stations, as well as those on the Mississippi and Ohio, had positive trends. The stations with negative trends were scattered throughout the state.

**Table 3. Median Cl<sup>-</sup> Values (mg/L) for Rivers in Illinois for Water Years 1991–1992 at USGS stations. For Rivers with More Than One Station (Ordered from Upstream to Downstream)**

<i>River</i>	<i>Location</i>	<i>Station</i>	<i>Median</i>	<i>River</i>	<i>Location</i>	<i>Station</i>	<i>Median</i>
Big Muddy	Murphysboro	5599500	31	La Moine	Colmar	5585000	17
Cache	Forman	3612000	10	Little Wabash	Effingham	3378635	30
Cal Sag Channel	Sag Bridge	5536700	105	Little Wabash	Carmi	3381495	34
Casey Fork	Mt Vernon	5595830	67	Lusk Ck	Eddyville	3384450	2.3
CSSC	Romeoville	5536995	109	Md Fk Vermilion	Oakwood	3336645	24
CSSC	Lockport	5537000	91	N Branch Chicago	Deerfield	5534500	131
Crab Orchard Ck	Carbondale	5598245	13	N Branch Chicago	Niles	5536000	146
Des Plaines	Riverside	5532500	158	N Fork Saline	Texas City	3382325	86
Des Plaines	Joliet	5537980	99	Pecatonica	Freeport	5435500	20
Embarras	Camargo	3343395	30	Richland Ck	Hecker	5595200	65
Embarras	Diona	3344000	29	Rock	Rockton	5437500	24
Embarras	Billett	3346550	30	Rock	Como	5443500	38
Fox	Channel Lk	5546700	65	S Fork Saline	Crab Orchard	3382055	32
Fox	S Elgin	5551000	75	S Fork Saline	Carrier Mills	3382100	19
Fox	Montgomery	5551540	85	Saline Branch	Mayview	3337700	51
Fox	Dayton	5552500	70	Salt Fork	St Joseph	3336900	39
Green	Geneseo	5447500	25	Sangamon	Allerton Park	5572125	44
Illinois	Marseilles	5543500	63	Sangamon	Oakford	5583000	34
Illinois	Peoria	5559900	59	Sangamon S Fork	Kincaid	5575500	50
Illinois	Valley City	5586100	52	Spoon	Seville	5570000	31
Iroquois	Chebanse	5526000	40	Sugar Ck (Saline)	Stonefort	3382090	5.9
Kankakee	Wilmington	5527500	27	Sugar Ck (Lk Springfield)	Springfield	5576250	56
Kaskaskia	Cooks Mills	5591200	33	Sugar Ck (Salt Ck)	Hartsburg	5581500	48
Kaskaskia	Venedy Station	5594100	27	Thorn Ck	Thornton	5536275	130
Kishwaukee	Perryville	5440000	43				

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**Table 4. Median CI Values (mg/L) for 2008 at River Stations Monitored by MWRDGC**

<i>Station</i>	<i>River</i>	<i>Location</i>	<i>CI</i>	<i>Station</i>	<i>River</i>	<i>Location</i>	<i>CI</i>
12	Buffalo Ck	Lake-Cook Rd	286	34	N Br Chicago	Dempster St	231
43	Cal-Sag Channel	Rte 83	186	37	N Br Chicago	Wilson Ave	166
58	Cal-Sag Channel	Ashland Ave	176	46	N Br Chicago	Grand Ave	159
59	Cal-Sag Channel	Cicero Ave	173	73	N Br Chicago	Diversey Ave	159
49	Calumet	Ewing St	33.5	96	N Br Chicago	Albany Ave	236
55	Calumet	130 <sup>th</sup> St	156	104	N Br Chicago	Glenview Rd	204
74	Calumet	Lake Shore Dr	45.5	31	N Br Chicago (Md Fk)	Lake-Cook Rd	277
100	Chicago	Wells St	105	103	N Br Chicago (W Fk)	Golf Rd	288
40	CSSC	Damen Ave	143	106	N Br Chicago (W Fk)	Dundee Rd	350
41	CSSC	Harlem Ave	175	35	N Shore Channel	Central Ave	21.5
42	CSSC	Rte 83	169	36	N Shore Channel	Touhy Ave	135
48	CSSC	Stephen St	167	101	N Shore Channel	Foster Ave	140
75	CSSC	Cicero	169	102	N Shore Channel	Oakton Ave	72.0
92	CSSC	Lockport	162	39	S Br Chicago	Madison St	134
13	Des Plaines	Lake-Cook Rd	182	108	S Br Chicago	Loomis St	136
17	Des Plaines	Oakton St	196	99	S Br Chicago (S Fk)	Archer Ave	170
19	Des Plaines	Belmont Ave	196	18	Salt Ck	Devon Ave	241
20	Des Plaines	Roosevelt Rd	195	24	Salt Ck	Wolf Rd	252
22	Des Plaines	Ogden Ave	197	79	Salt Ck	Higgins Rd	388
23	Des Plaines	Willow Springs Rd	209	80	Salt Ck	Arlington Hts Rd	235
29	Des Plaines	Stephen St	198	90	Salt Ck	Rte 19	252
91	Des Plaines	Material Service Rd	193	109	Salt Ck	Brookfield Ave	256
86	Grand Calumet	Burnham Ave	138	32	Skokie	Lake-Cook Rd	247
77	Higgins Ck	Elmhurst Rd	452	105	Skokie	W Frontage Rd	181
78	Higgins Ck	Wille Rd	187	54	Thorn Ck	Joe Orr Rd	160
52	Little Calumet	Wentworth Ave	168	97	Thorn Ck	170 <sup>th</sup> St	182
56	Little Calumet	Indiana Ave	172	64	W Br DuPage	Lake St	168
57	Little Calumet	Ashland Ave	191	89	W Br DuPage	Walnut Ln	151
76	Little Calumet	Halsted Ave	170	110	W Br DuPage	Springinsguth Rd	297
				50	Wolf Lake	127 <sup>th</sup> St	64.9

**Table 5. Trends Determined by Kendall Tau Statistic and  $\beta_1$  Values (Reported as Yearly Change in CI) for MWRDGC Stations with Monitoring Data from 1975 to 2008. Kendall Tau Significance Determined at 95% Confidence Level.  $\beta_1$  Values Reported for All Data (total) as Well as Seasonally.**

Station	River	Kendall Tau	$\beta_1$ (mg/L/yr)				
		Significant?	Total	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
12	Buffalo Creek	Y	5.8	13.2	6.9	1.4	3.0
13	Des Plaines R	Y	3.4	6.9	3.4	2.1	2.0
17	Des Plaines R	Y	3.8	8.2	3.9	2.6	2.7
18	Salt Creek	Y	2.1	6.7	6.4	-0.1	-1.2
19	Des Plaines R	Y	3.7	8.2	3.4	1.6	2.8
20	Des Plaines R	Y	4.1	8.6	3.7	2.2	3.0
22	Des Plaines R	Y	3.3	2.6	3.8	1.2	1.2
23	Des Plaines R	Y	3.4	8.9	4.0	1.1	2.0
24	Salt Creek	N					
29	Des Plaines R	Y	3.3	8.7	3.8	1.0	1.5
31	N Branch Chicago R (Md Fk)	Y	5.2	7.1	5.9	4.8	3.5
32	Skokie R	Y	4.6	5.5	6.3	4.3	3.5
34	N Branch Chicago R	Y	5.5	9.7	6.3	3.5	3.9
35	N Shore Channel	Y	0.17	5.4	2.0	-0.3	0.3
36	N Shore Channel	Y	1.9	5.2	2.1	0.9	2.7
37	N Branch Chicago R	Y	2.7	6.8	2.9	1.3	3.4
39	S Branch Chicago R	Y	2.6	6.4	2.5	0.5	3.0
40	CSSC	Y	2.7	6.4	2.7	0.4	3.2
41	CSSC	Y	2.5	5.2	2.2	1.0	4.2
42	CSSC	Y	2.7	7.0	2.4	1.1	2.3
43	Cal-Sag Channel	Y	1.4	5.2	1.8	0.1	0.0
46	N Branch Chicago R	Y	2.7	6.8	3.2	1.4	2.7
48	CSSC	Y	2.4	5.2	2.5	0.9	1.9
49	Calumet R	Y	0.76	1.7	0.5	-0.1	0.8
50	Wolf Lake	Y	0.51	0.4	0.7	0.6	0.4
52	Little Calumet R	Y	1.9	3.6	2.5	0.4	0.5
54	Thorn Creek	Y*	-4.8	-1.3	-2.8	-6.1	-7.7
55	Calumet R	N					
56	Little Calumet R	N					
57	Little Calumet R	Y	0.07	5.2	1.8	-2.3	-2.5
58	Cal-Sag Channel	Y	1.2	5.0	0.9	-0.1	1.4
59	Cal-Sag Channel	Y	1.2	4.3	1.8	-0.2	0.2
64	W Branch DuPage R	Y	-0.93	4.4	1.7	-2.2	-3.1
73	N Branch Chicago R	Y	2.5	6.7	2.5	1.0	2.6
74	Chicago R	Y	1.1	6.0	2.7	0.0	1.4
75	CSSC	Y	2.9	7.0	1.5	0.6	3.3
76	Little Calumet R	Y	1.4	4.7	10.1	0.6	1.4
78	Higgins Creek	Y	1.6	3.8	9.9	1.0	1.4
79	Salt Creek	Y	7.3	15.9	6.4	5.8	4.6
80	Salt Creek	Y	2.0	6.6	2.3	0.3	-0.6
90	Salt Creek	Y	6.8	12.8	11.1	4.4	3.7

\* Negative trend.

**Table 6. Trends Determined by Kendall Tau Statistic and  $\beta_1$  Values (Reported as Yearly Change in CI, mg/L/yr) for USGS Stations. Data Start in 1984, and End between 1997 and 2008. Kendall Tau Significance Determined at 95% Confidence.**

Station	River	KT sign.	$\beta_1$	Station	River	KT sign.	$\beta_1$
5532000	Addison Creek	Y	9.33	3384450	Lusk Creek	N	
5599500	Big Muddy	N		3336645	Middle Fork Vermilion	N	
3378000	Bonpas Creek	Y*	-1.08	7022000	Mississippi	Y	0.21
3612000	Cache	Y*	0.07	5587455	Mississippi	Y	0.48
5536700	Cal Sag Channel	N		5534500	N Branch Chicago	Y	7.13
5595830	Casey Fork	N		5536000	N Branch Chicago	Y	5.74
5598245	Crab Orchard Creek	N		3346000	N Fork Embarras	Y*	-2.00
5593520	Crooked Creek	Y*	-3.17	3382325	N Fork Saline	N	
5537000	CSSC	Y	3.84	3338780	N Fork Vermilion	Y*	-0.29
5536995	CSSC	Y	5.64	3612500	Ohio	Y	0.23
5528000	Des Plaines	Y	6.00	5435500	Pecatonica	Y*	-0.15
5529000	Des Plaines	Y	6.03	5550500	Poplar Creek	Y	14.2
5532500	Des Plaines	Y	2.11	5595200	Richland Creek	Y	0.99
5537980	Des Plaines	N		5437500	Rock	Y	1.00
5540500	DuPage	Y*	-2.63	5443500	Rock	Y	0.99
3344000	Embarras	N		5446500	Rock	Y	0.98
3345500	Embarras	Y*	-0.40	3337700	Saline Branch	Y	1.63
3343395	Embarras	N		5531500	Salt Creek	N	
3346550	Embarras	N		3336900	Salt Fork	N	
5551000	Fox	Y	5.89	5576500	Sangamon	N	
5551540	Fox	Y	7.11	5583000	Sangamon	Y	0.58
5552500	Fox	Y	1.76	5572000	Sangamon	N	
5550000	Fox	Y	5.56	5573540	Sangamon	N	
5546700	Fox	Y	2.94	5572125	Sangamon	N	
5447500	Green	N		3382100	S Fork Saline	N	
5539000	Hickory Creek	Y	6.52	3382055	S Fork Saline	N	
5543500	Illinois	Y	1.24	5575500	S Fork Sangamon	N	
5559900	Illinois	Y	2.54	3380500	Skillet Fork	N	
5586100	Illinois	Y	0.90	5594450	Silver Creek	Y	2.04
5526000	Iroquois	Y	0.32	5594800	Silver Creek	N	
5520500	Kankakee	Y	0.36	3382090	Sugar Creek	Y*	-0.59
5527500	Kankakee	Y	0.07	5576250	Sugar Creek	Y	2.53
5594100	Kaskaskia	N		5581500	Sugar Creek	Y	1.18
5592500	Kaskaskia	Y*	-2.08	5536275	Thorn Creek	N	
5591200	Kaskaskia	Y	1.68	3339000	Vermilion	N	
5440000	Kishwaukee	Y	0.98	5539900	W Branch DuPage	Y	4.23
5584500	La Moine	N		5540095	W Branch DuPage	N	
5585000	La Moine	N					
3378635	Little Wabash	N					
3379500	Little Wabash	N					
3381495	Little Wabash	N					

\* Negative trend.

**ATTACHMENT 4  
 LEMONT REFINERY CHLORIDE CONTRIBUTION ON DAYS WHEN SHIP CANAL CONTAINS MORE THAN 500 mg/L CHLORIDES**

Date	Influent			Effluent			Ship and Sanitary Canal					
	Flow Rate (MGD)	Measured Chloride Concentration (ppm)	Chloride Mass Loading (lb/day)	Flow Rate (MGD)	Measured Chloride Concentration (ppm)	Chloride Mass Loading (lb/day)	Net Chloride Mass Loading (lb/day)	Flow Rate (MGD)	Measured Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
<b>Average</b>	<b>7.093</b>	<b>645</b>	<b>38,409</b>	<b>5.813</b>	<b>1063</b>	<b>51,344</b>	<b>12,935</b>	<b>1399</b>	<b>645</b>	<b>7,425,991</b>	<b>647</b>	<b>0.18%</b>

**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Net Chloride Mass Loading (lb/day)	Ship and Sanitary Canal				
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)		Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
	$Q_{in}$	$C_{in}$	$R_{m,in}$	$Q_{eff}$	$C_{eff}$	$R_{m,eff}$	$R_{m,net}$	$Q_0$	$C_0 = C_{in}$	$R_{m,0}$	$C_1$	$F_{net/0}$
12/01/12	6.949	121	7,016	5.125	770	32,928	25,912	621	121	627,003	126	4.13%
12/02/12	7.069	121	7,138	4.729	770	30,388	23,250	509	121	513,921	127	4.52%
12/03/12	7.013	121	7,081	2.691	770	17,287	10,207	751	121	758,260	123	1.35%
12/04/12	7.059	121	7,127	1.725	770	11,086	3,959	856	121	864,275	122	0.46%
12/05/12	7.173	130	7,781	3.535	765	22,554	14,772	530	130	574,926	134	2.57%
12/06/12	7.178	139	8,325	3.185	759	20,172	11,847	615	139	713,317	142	1.66%
12/07/12	7.187	137	8,228	3.316	758	20,978	12,750	615	137	704,080	141	1.81%
12/08/12	6.552	135	7,403	4.609	757	29,129	21,726	542	135	612,366	141	3.55%
12/09/12	6.216	134	6,929	3.788	757	23,914	16,985	858	134	956,504	136	1.78%
12/10/12	6.204	132	6,823	3.640	756	22,958	16,135	850	132	934,818	134	1.73%
12/11/12	6.103	130	6,620	4.521	755	28,483	21,862	785	130	851,542	134	2.57%
12/12/12	6.218	138	7,134	5.100	814	34,620	27,485	764	138	876,575	142	3.14%
12/13/12	6.079	145	7,355	6.266	872	45,591	38,236	744	145	900,189	151	4.25%
12/14/12	6.275	141	7,373	4.753	844	33,466	26,094	689	141	809,496	146	3.22%
12/15/12	6.261	137	7,137	3.662	816	24,923	17,786	707	137	805,866	140	2.21%
12/16/12	6.415	132	7,088	4.038	787	26,531	19,443	676	132	746,840	136	2.60%
12/17/12	6.276	128	6,714	3.620	759	22,935	16,221	805	128	861,146	131	1.88%
12/18/12	6.197	124	6,412	3.511	731	21,415	15,003	815	124	843,281	127	1.78%
12/19/12	6.194	129	6,642	3.405	743	21,113	14,471	603	129	646,567	132	2.24%
12/20/12	6.351	133	7,048	3.405	755	21,454	14,406	2790	133	3,096,340	134	0.47%
12/21/12	6.379	129	6,854	4.642	803	31,105	24,251	1902	129	2,043,387	130	1.19%
12/22/12	6.703	125	6,964	5.610	851	39,836	32,872	1426	125	1,481,432	127	2.22%
12/23/12	6.962	120	6,986	5.628	899	42,217	35,231	1596	120	1,601,441	123	2.20%
12/24/12	6.889	116	6,668	5.526	947	43,669	37,001	1121	116	1,085,067	120	3.41%
12/25/12	7.089	116	6,842	5.225	871	37,973	31,131	916	116	884,090	120	3.52%
12/26/12	7.087	115	6,821	5.388	795	35,741	28,921	754	115	725,636	120	3.99%
12/27/12	7.001	115	6,718	5.388	719	32,328	25,610	863	115	828,136	119	3.09%
12/28/12	6.988	118	6,904	5.389	716	32,216	25,312	875	118	864,475	122	2.93%
12/29/12	6.833	122	6,945	5.801	714	34,552	27,607	464	122	471,583	129	5.85%
12/30/12	6.731	125	7,032	5.623	711	33,370	26,339	888	125	927,706	129	2.84%

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**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Ship and Sanitary Canal					
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Net Chloride Mass Loading (lb/day)	Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
--	Q <sub>in</sub>	C <sub>in</sub>	R <sub>m,in</sub>	Q <sub>eff</sub>	C <sub>eff</sub>	R <sub>m,eff</sub>	R <sub>m,net</sub>	Q <sub>0</sub>	C <sub>0</sub> = C <sub>in</sub>	R <sub>m,0</sub>	C <sub>1</sub>	F <sub>net/0</sub>
12/31/12	6.906	129	7,410	5.519	709	32,630	25,220	792	129	849,883	133	2.97%
01/01/13	7.052	132	7,767	5.431	706	31,996	24,229	702	132	773,221	136	3.13%
01/02/13	7.047	136	7,968	5.077	719	30,462	22,495	785	136	887,568	139	2.53%
01/03/13	7.044	139	8,171	4.638	732	28,330	20,159	580	139	672,722	144	3.00%
01/04/13	7.067	142	8,397	4.628	738	28,500	20,103	600	142	712,942	147	2.82%
01/05/13	7.026	146	8,548	4.625	744	28,714	20,166	379	146	461,094	153	4.37%
01/06/13	6.955	149	8,659	4.617	750	28,895	20,235	674	149	839,115	153	2.41%
01/07/13	7.114	153	9,058	4.532	756	28,592	19,534	813	153	1,035,233	156	1.89%
01/08/13	7.069	156	9,202	4.421	762	28,111	18,909	764	156	994,514	160	1.90%
01/09/13	7.092	159	9,380	4.194	764	26,721	17,341	823	159	1,088,484	162	1.59%
01/10/13	7.226	161	9,708	4.454	765	28,431	18,723	582	161	781,883	166	2.39%
01/11/13	7.181	141	8,473	3.944	755	24,848	16,374	1733	141	2,044,753	143	0.80%
01/12/13	7.050	122	7,165	4.969	745	30,889	23,724	1623	122	1,649,524	124	1.44%
01/13/13	7.043	102	6,007	5.965	735	36,583	30,577	1380	102	1,176,855	105	2.60%
01/14/13	6.766	83	4,663	5.610	725	33,940	29,277	1022	83	704,407	86	4.16%
01/15/13	6.876	63	3,615	5.363	715	31,996	28,381	753	63	395,848	68	7.17%
01/16/13	6.778	109	6,137	5.354	740	33,060	26,923	924	109	836,555	112	3.22%
01/17/13	7.005	154	9,001	5.289	765	33,763	24,762	874	154	1,123,117	158	2.20%
01/18/13	7.077	154	9,118	5.058	777	32,787	23,669	586	154	754,984	160	3.14%
01/19/13	7.099	155	9,170	5.069	789	33,353	24,183	728	155	940,362	159	2.57%
01/20/13	7.372	155	9,547	5.650	800	37,735	28,188	872	155	1,129,278	159	2.50%
01/21/13	7.081	156	9,193	5.189	812	35,164	25,971	728	156	945,222	160	2.75%
01/22/13	6.947	156	9,043	5.044	824	34,681	25,638	673	156	876,057	161	2.93%
01/23/13	6.975	160	9,312	4.858	812	32,915	23,603	526	160	702,261	166	3.36%
01/24/13	7.241	164	9,909	4.886	800	32,619	22,711	641	164	877,192	169	2.59%
01/25/13	7.281	162	9,867	4.656	805	31,284	21,418	845	162	1,145,079	166	1.87%
01/26/13	7.379	161	9,901	4.649	810	31,440	21,539	564	161	756,760	166	2.85%
01/27/13	7.227	159	9,601	4.646	816	31,619	22,018	742	159	985,689	163	2.23%
01/28/13	7.282	158	9,576	4.983	821	34,130	24,554	1693	158	2,226,414	160	1.10%
01/29/13	7.169	156	9,331	5.521	826	38,050	28,719	2643	156	3,440,445	157	0.83%

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**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Ship and Sanitary Canal					
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Net Chloride Mass Loading (lb/day)	Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
--	$Q_{in}$	$C_{in}$	$R_{m,in}$	$Q_{eff}$	$C_{eff}$	$R_{m,eff}$	$R_{m,net}$	$Q_0$	$C_0 = C_{in}$	$R_{m,0}$	$C_1$	$F_{net/0}$
01/30/13	6.692	218	12,173	5.512	844	38,816	26,643	4025	218	7,321,755	219	0.36%
01/31/13	5.185	280	12,113	6.431	862	46,260	34,146	2837	280	6,628,423	281	0.52%
02/01/13	5.353	265	11,854	7.105	824	48,830	36,976	1783	265	3,948,618	268	0.94%
02/02/13	5.408	251	11,318	5.265	785	34,494	23,176	1920	251	4,018,108	252	0.58%
02/03/13	5.325	236	10,494	5.833	747	36,352	25,857	1210	236	2,384,834	239	1.08%
02/04/13	5.240	222	9,689	6.031	708	35,647	25,958	1121	222	2,072,852	224	1.25%
02/05/13	5.276	207	9,113	5.591	670	31,257	22,144	1221	207	2,109,011	209	1.05%
02/06/13	7.003	246	14,345	6.227	688	35,747	21,402	638	246	1,306,968	250	1.64%
02/07/13	7.344	284	17,405	6.004	706	35,373	17,968	1324	284	3,137,611	286	0.57%
02/08/13	7.231	341	20,575	5.941	735	36,428	15,853	2127	341	6,052,220	342	0.26%
02/09/13	7.311	398	24,280	6.090	764	38,801	14,521	1518	398	5,041,360	399	0.29%
02/10/13	7.464	455	28,340	6.098	792	40,320	11,980	1470	455	5,581,123	456	0.21%
02/11/13	7.20	512	30,761	6.20	821	42,456	11,696	2470	512	10,552,607	513	0.11%
02/12/13	6.34	569	30,102	5.37	850	38,088	7,986	1771	569	8,408,599	570	0.09%
02/13/13	6.38	605	32,195	6.42	882	47,282	15,088	1337	605	6,744,046	606	0.22%
02/14/13	6.56	640	35,042	6.61	914	50,378	15,336	1319	640	7,043,972	641	0.22%
02/15/13	6.32	587	30,959	5.32	937	41,639	10,680	874	587	4,280,972	589	0.25%
02/16/13	6.43	534	28,668	3.79	960	30,402	1,734	918	534	4,090,504	536	0.04%
02/17/13	6.355	481	25,508	4.490	984	36,855	11,348	939	481	3,768,804	483	0.30%
02/18/13	6.461	428	23,076	4.503	1007	37,827	14,751	1017	428	3,632,098	431	0.41%
02/19/13	6.687	375	20,924	4.953	1030	42,566	21,642	1300	375	4,067,874	377	0.53%
02/20/13	6.438	350	18,801	5.950	1065	52,851	34,050	856	350	2,499,969	355	1.36%
02/21/13	6.571	325	17,820	5.622	1099	51,555	33,735	871	325	2,362,079	330	1.43%
02/22/13	6.599	317	17,444	5.615	1100	51,521	34,077	1133	317	2,995,077	321	1.14%
02/23/13	6.762	309	17,413	5.450	1100	50,029	32,616	814	309	2,096,106	314	1.56%
02/24/13	7.470	300	18,725	5.065	1101	46,523	27,798	696	300	1,744,625	306	1.59%
02/25/13	7.706	292	18,790	5.519	1101	50,726	31,936	884	292	2,155,387	297	1.48%
02/26/13	7.542	284	17,873	5.515	1102	50,711	32,838	1247	284	2,955,137	288	1.11%
02/27/13	7.946	351	23,273	5.517	1077	49,582	26,309	1247	351	3,652,300	354	0.72%
02/28/13	7.662	418	26,725	5.670	1052	49,772	23,046	1907	418	6,651,503	420	0.35%

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**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Ship and Sanitary Canal					Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Net Chloride Mass Loading (lb/day)	Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	
--	Q <sub>in</sub>	C <sub>in</sub>	R <sub>m,in</sub>	Q <sub>eff</sub>	C <sub>eff</sub>	R <sub>m,eff</sub>	R <sub>m,net</sub>	Q <sub>0</sub>	C <sub>0</sub> = C <sub>in</sub>	R <sub>m,0</sub>	C <sub>1</sub>	F <sub>net/0</sub>
03/01/13	7.445	466	28,961	6.016	1078	54,096	25,135	1273	466	4,952,147	469	0.51%
03/02/13	7.57	514	32,501	6.17	1103	56,769	24,268	1285	514	5,515,653	517	0.44%
03/03/13	7.70	563	36,132	6.16	1129	58,045	21,913	1173	563	5,506,689	566	0.40%
03/04/13	7.59	611	38,672	6.16	1154	59,332	20,660	671	611	3,419,908	616	0.60%
03/05/13	7.61	659	41,839	5.71	1180	56,175	14,336	1393	659	7,660,011	661	0.19%
03/06/13	7.59	685	43,411	5.53	1243	57,325	13,914	1095	685	6,258,893	688	0.22%
03/07/13	7.86	711	46,654	5.57	1306	60,736	14,082	1111	711	6,591,382	714	0.21%
03/08/13	8.08	659	44,438	5.79	1285	62,065	17,627	1425	659	7,833,598	661	0.23%
03/09/13	7.90	607	39,971	5.79	1264	61,100	21,129	1144	607	5,790,569	610	0.36%
03/10/13	8.01	554	37,056	6.02	1244	62,503	25,447	4501	554	20,822,126	555	0.12%
03/11/13	5.91	502	24,745	7.47	1223	76,231	51,486	5007	502	20,982,012	503	0.25%
03/12/13	6.044	450	22,695	7.882	1202	79,056	56,360	3482	450	13,074,772	452	0.43%
03/13/13	6.169	374	19,251	7.674	1098	70,306	51,055	2333	374	7,280,801	376	0.70%
03/14/13	5.973	298	14,851	7.153	994	59,331	44,480	2336	298	5,808,740	300	0.77%
03/15/13	6.160	318	16,347	6.942	998	57,811	41,465	2122	318	5,630,738	320	0.74%
03/16/13	5.972	338	16,845	6.875	1002	57,479	40,634	1759	338	4,961,070	341	0.82%
03/17/13	6.053	358	18,082	6.672	1006	56,004	37,922	1392	358	4,158,293	361	0.91%
03/18/13	6.100	378	19,240	6.689	1010	56,372	37,132	1659	378	5,232,763	381	0.71%
03/19/13	6.005	398	19,942	7.086	1014	59,952	40,010	1651	398	5,483,060	401	0.73%
03/20/13	7.806	337	21,919	6.163	1021	52,510	30,590	954	337	2,678,714	341	1.14%
03/21/13	7.851	275	18,016	5.815	1028	49,878	31,861	774	275	1,776,096	281	1.79%
03/22/13	7.715	276	17,794	5.804	1026	49,705	31,911	1099	276	2,534,712	280	1.26%
03/23/13	7.508	278	17,403	5.938	1025	50,778	33,375	936	278	2,169,706	283	1.54%
03/24/13	7.592	279	17,688	5.945	1023	50,754	33,066	821	279	1,912,720	285	1.73%
03/25/13	7.425	281	17,386	5.705	1022	48,635	31,249	769	281	1,800,557	286	1.74%
03/26/13	7.539	282	17,740	5.417	1020	46,107	28,366	797	282	1,875,427	287	1.51%
03/27/13	7.375	314	19,292	5.934	1128	55,850	36,558	1208	314	3,160,074	318	1.16%
03/28/13	7.508	345	21,614	5.333	1236	55,007	33,393	708	345	2,038,192	352	1.64%
03/29/13	7.945	345	22,873	4.785	1236	49,353	26,479	677	345	1,948,950	351	1.36%
03/30/13	7.908	345	22,764	4.647	1236	47,931	25,167	1158	345	3,333,654	349	0.75%

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**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Net Chloride Mass Loading (lb/day)	Ship and Sanitary Canal				
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)		Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
	$Q_{in}$	$C_{in}$	$R_{m,in}$	$Q_{eff}$	$C_{eff}$	$R_{m,eff}$		$R_{m,net}$	$C_0 = C_{in}$	$R_{m,0}$	$C_1$	$F_{net/0}$
03/31/13	7.954	345	22,899	4.923	1236	50,777	27,877	806	345	2,320,315	350	1.20%

**ATTACHMENT 4  
LEMONT REFINERY CHLORIDE CONTRIBUTION TO SHIP CANAL BY DAY**

Date	Influent to Citgo			Effluent from Citgo			Net Chloride Mass Loading (lb/day)	Ship and Sanitary Canal				
	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)	Flow Rate (MGD)	Chloride Concentration for Calculation (ppm)	Chloride Mass Flow Rate (lb/day)		Flow Rate (MGD)	Upstream Chloride Concentration (ppm)	Upstream Chloride Mass Flow Rate (lb/day)	Downstream Chloride Concentration (ppm)	Ratio of Net Chloride Mass Loading to Upstream Chloride Mass Flow Rate (%)
--	<i>Q<sub>in</sub></i>	<i>C<sub>in</sub></i>	<i>R<sub>m,in</sub></i>	<i>Q<sub>eff</sub></i>	<i>C<sub>eff</sub></i>	<i>R<sub>m,eff</sub></i>	<i>R<sub>m,net</sub></i>	<i>Q<sub>0</sub></i>	<i>C<sub>0</sub> = C<sub>in</sub></i>	<i>R<sub>m,0</sub></i>	<i>C<sub>1</sub></i>	<i>F<sub>net/0</sub></i>

**Notes:**

a) Gray, italicized font indicates results based on interpolated concentration value. Normal font indicates results based on concentration measured during that day.

b) Chicago Ship and Sanitary Canal flow rate data was obtained from the *USGS National Water Information System: Web Interface* on June 6, 2013 for the Lemont, Illinois flow meter (ID: 05536890) [http://waterdata.usgs.gov/il/nwis/uv/?site\\_no=05536890&agency\\_cd=USGS](http://waterdata.usgs.gov/il/nwis/uv/?site_no=05536890&agency_cd=USGS)

**Calculation Method:**

$$R_{m,in} \text{ (lb/day)} = Q_{in} \text{ (MGD)} \times C_{in} \text{ (ppm)} \times (10^6 \text{ gal/MG}) \times (3.785 \text{ L/gal}) \times (1 \text{ mg/L} / \text{ppm}) / (1000 \text{ mg/g}) / (453.6 \text{ g/lb})$$

$$R_{m,eff} \text{ (lb/day)} = Q_{eff} \text{ (MGD)} \times C_{eff} \text{ (ppm)} \times (10^6 \text{ gal/MG}) \times (3.785 \text{ L/gal}) \times (1 \text{ mg/L} / \text{ppm}) / (1000 \text{ mg/g}) / (453.6 \text{ g/lb})$$

$$R_{m,0} \text{ (lb/day)} = Q_0 \text{ (MGD)} \times C_0 \text{ (ppm)} \times (10^6 \text{ gal/MG}) \times (3.785 \text{ L/gal}) \times (1 \text{ mg/L} / \text{ppm}) / (1000 \text{ mg/g}) / (453.6 \text{ g/lb})$$

$$C_0 \text{ (ppm)} = C_{in} \text{ (ppm)}$$

$$R_{m,net} \text{ (lb/day)} = R_{m,eff} \text{ (lb/day)} - R_{m,in} \text{ (lb/day)}$$

$$F_{net/0} \text{ (%) } = [R_{m,net} \text{ (lb/day)}] / [R_{m,0} \text{ (lb/day)}] \times 100\%$$

$$C_1 \text{ (ppm)} = [R_{m,0} + R_{m,net} \text{ (lb/day)}] / [Q_0 + Q_{eff} - Q_{in} \text{ (MGD)}] / (10^6 \text{ gal/MG}) * (453.6 \text{ g/lb}) * (1000 \text{ mg/g}) \times (1 \text{ ppm} / \text{mg/L})$$

**ATTACHMENT 5**  
**CITGO CHLORIDE CONTRIBUTION TO CSSC DURING WINTER MONTHS**  
**WHEN UPSTREAM CHLORIDES EXCEED 500 mg/L**

Net contribution of chlorides from Lemont Refinery based on days when chlorides upstream exceed  
500 mg/L 12,935 lbs/day

(From 2012 data)

% of days upstream chlorides exceed 500 mg/L in winter

November -April 10.20% of 180 days  
or 18.36 days

From Citgo influent data 2007 to 2013 data

**Net Contribution from Citgo 237,487 pounds per year**  
**119 Tons per year**

**CERTIFICATE OF SERVICE**

I, the undersigned, certify that on November 22, 2013, I served electronically the attached  
**Pre-Filed Testimony of: Larry Tyler, Bruce Nelson, Roger Klocek and James Huff**, upon  
the following:

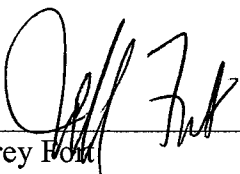
John Therriault, Clerk  
Pollution Control Board  
James R. Thompson Center  
100 West Randolph St., Suite 11-500  
Chicago, IL 60601

and by U.S. Mail, first class postage prepaid, to the following persons:

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