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Innovative Approaches to Complying with Very Low National Pollutant Discharge Elimination System (NPDES) Permit Limits for Metals

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ABSTRACT

The NPDES permit issued to the Savannah River Site (SRS) in 2003 contained very low metals limits for several outfalls. Copper, lead and zinc limits were as low as seven micrograms per liter (7 ug/l), 1 ug/l, and 100 ug/l, respectively. The permit contained compliance schedules that provided SRS with only three to five years to select and implement projects that would enable outfall compliance. Discharges from a few outfalls were eliminated or routed into other locations relatively inexpensively. However, some outfall problems were much more difficult to correct. SRS personnel implemented several innovative projects in order to meet compliance schedule deadlines as inexpensively as possible. These innovations included (1) connecting several outfall discharges to the site's Central Sanitary Wastewater Treatment Facility (CSWTF), (2) constructing a treatment wetlands and completing a water-effects ratio (WER) on its effluent, (3) installing a stannous chloride feed system to remove mercury in an existing air stripper, and (4) constructing a humic acid feed system to increase effluent dissolved organic carbon (DOC) content and take advantage of biotic ligand modeling to raise effluent limits.

KEYWORDS

NPDES, biotic ligand model (BLM), water-effects ratio (WER), copper, lead, zinc, dissolved organic carbon (DOC)

INTRODUCTION

SRS is a nearly sixty year old Department of Energy (DOE) facility located on a 310 square mile tract of land near Aiken, South Carolina. Situated in the Savannah River watershed, many of the industrial facilities scattered throughout the Site discharge wastewater into headwater streams that carry surface water only during rain events. These ephemeral streams are classified as waters of the State of South Carolina and must meet the same water quality standards as perennial streams. Typically, the 7Q10 (low flow condition) of these streams is zero. Thus, they provide no blending when NPDES permit limitations are calculated. The result is very low NPDES permit limits for hardness dependent metals such as copper, lead and zinc.

The SRS NPDES permit was issued by the South Carolina Department of Health and Environmental Control (SCDHEC) in 2003 and contained very stringent limits for copper, lead and zinc at several outfalls. The limits shown in Table 1 were typical.

Table 1. Example stringent NPDES permit effluent limits

Effluent Parameter	Discharge Limitations (micrograms per liter)	
	Monthly Average	Daily Maximum
Lead, total	1.0	20.0
Zinc, total	---	100.0
Copper, total	7.0	9.0
Mercury, total	0.051	0.14

Usually, compliance schedules in SCDHEC-issued NPDES permits are three years or less in length. Due to the number of SRS outfalls expected to require expensive corrective measures, SCDHEC issued the SRS NPDES permit with three, four and five year compliance schedules. SRS formed a project team to evaluate the extent of outfall problems, consider alternatives, and make recommendations to management and DOE. Approved alternatives were evaluated in depth and the costs of implementing them were estimated. Initially, the total cost for twelve outfall projects was estimated to be in excess of twenty-five million dollars. Between federal budget cuts and the need to use available funding on facility decontamination and decommissioning, it became apparent that less expensive compliance alternatives must be discovered, where feasible.

A few outfalls were eliminated due to closure of the facilities discharging into them or by rerouting facility effluents into other processes or outfalls. For example, one low-flow outfall was eliminated simply by connecting a steam condensate line to a nearby cooling water system. Two other outfalls were eliminated by routing their effluents into wet ash basins that already received similar wastewater. Unfortunately, simple and inexpensive fixes were available for only a few such outfalls. Finding compliance alternatives for several others wasn't so easy.

METHODOLOGIES

Compliance alternatives remained to be found for six SRS outfalls. Three of the six discharged fairly low volumes of relatively clean water (clean water outfalls). The fourth outfall was associated with operating facilities that have a long-term future mission (long-term outfall). The fifth outfall contained low-level mercury and was associated with an air stripper that operates twenty-four hours a day treating groundwater under a Resource Conservation and Recovery Act

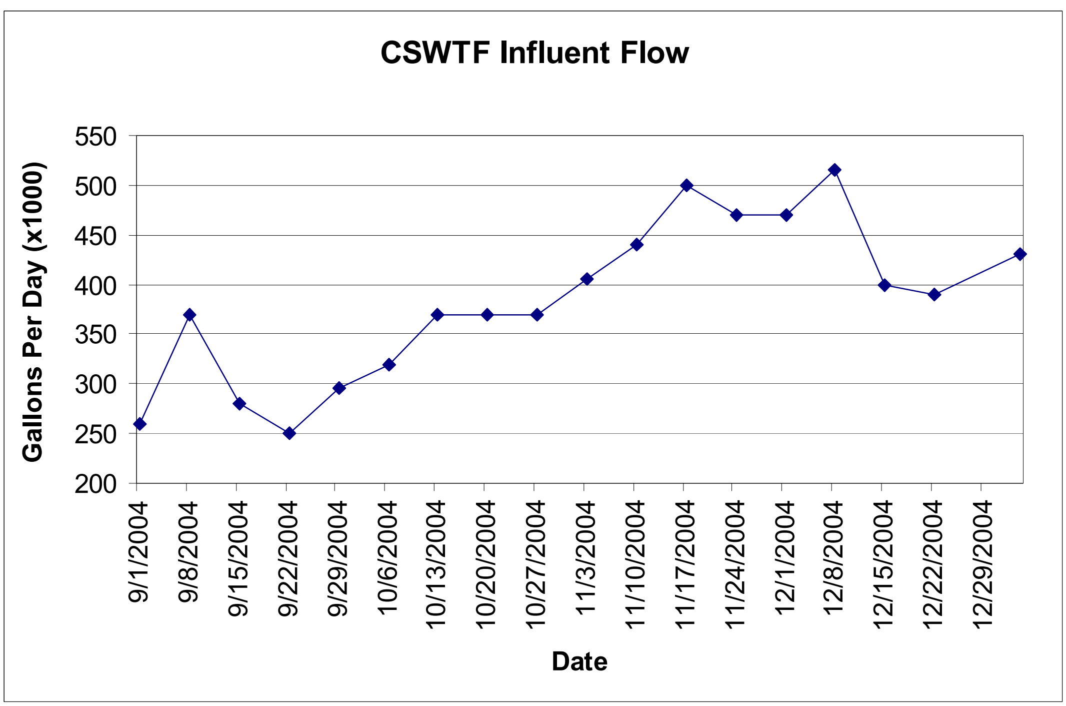
(RCRA) permit (air stripper outfall). The sixth was a high volume discharge with copper and zinc concentrations that barely exceeded future NPDES permit limits (low metal concentration outfall). Due to the differences in volumes and metals concentrations between these six discharges, each required its own innovative solution.

Sanitary Wastewater Treatment for Clean Water Outfalls

Sanitary wastewater generated across most of SRS is treated onsite within a centralized wastewater treatment facility. This Central Sanitary Wastewater Treatment Facility (CSWTF) receives human sewage that contains very little industrial input. During many years of operation the addition of cooling water-type discharges into the CSWTF had been resisted based upon the fear that too much "clean" water would upset the treatment process.

Three of the SRS outfalls with new metals limits released relatively low volumes of "clean" water (cooling tower blowdown, steam condensate, etc.). The cost to implement individual projects to bring these outfalls in compliance with new NPDES permit limits was much greater than the cost to connect them to the CSWTF collection system, which would eliminate the outfalls completely. Therefore, this option was explored in detail. In order to alleviate fears of upsetting the treatment system, a study was undertaken whereby roughly 160,000 gallons per day of clean water was routed into the CSWTF over a three month time span. This water was in addition to an average of 250,000 gallons per day of sewage that was already treated. The flow was increased gradually over the study period while operation of the treatment plant was observed carefully (Figure 1).

Figure 1. CSWTF clean water influent flow rate



Sludge volume indices, sludge settling rates, and effluent quality were unchanged during the study. Microscopic examination of activated sludge indicated that floc formation remained adequate and that protozoa were prolific. Dewatered sludge was unchanged. Overall, the study was very successful and indicated that the CSWTF should have no trouble handling additional sources of “clean” wastewater that contained very little biochemical oxygen demand. The decision was made to route the three low-flow outfalls into the CSWTF rather than trying to treat the wastewater from each outfall individually.

Wetland Treatment for Long-term Outfall

SRS personnel knew from experience that wetlands, constructed in accordance with certain design parameters, could remove metals such as copper, lead, zinc and mercury to low ug/l ranges. In the late 1990s, SRS constructed a treatment wetland to remove low levels of copper and mercury from a Savannah River National Laboratory discharge. After a reasonable “grow-in” period, wetland performance was excellent. Unfortunately, due to regulatory changes, the copper limit in the subsequent NPDES Permit was reduced to a level that the wetland effluent could not attain consistently. A WER study was completed successfully on the wetland effluent, enabling the copper limit to be maintained at a higher, achievable value.

Using this experience, SRS personnel requested approval from SCDHEC for a compliance option that included construction of a treatment wetland followed by a WER study on its effluent. This work was to be undertaken on effluent from tritium production facilities. These facilities have a long-term future and needed a long-term plan for compliance with the NPDES permit. SCDHEC issued a construction permit for the wetland and later established higher copper and lead NPDES permit limits based upon the WER. From beginning to end, the process required four years to complete. Figure 2 is an aerial view of the constructed wetland.

Figure 2. Tritium facilities constructed wetland wastewater treatment facility

Mercury Treatment for Air Stripper Outfall

In this particular outfall, roughly one-half million gallons per day of groundwater are passed through an air stripper that removes trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene, or PCE). Mercury is also present in the groundwater exiting the stripper. The reason for the presence of mercury is unclear since there has never been any known mercury contamination in the area. The mercury NPDES permit limit of fifty-one nanograms per liter (51 ng/l) was attained consistently without additional treatment until late in the life of the four-year compliance schedule for this outfall. It is believed that a process placed online to help remove TCE and PCE from the vadose zone of the groundwater was the reason for an unexpected increase in outfall mercury. Since source reduction was not possible, and because the mercury level had risen so late in the life of the compliance schedule, a treatment solution had to be designed, engineered and installed in a matter of months.

Scientists from the SRS Savannah River National Laboratory (SNRL) were knowledgeable in the laboratory method used for the analysis of low level mercury in aqueous systems. The method uses stannous chloride to reduce mercury to its elemental form and enable it to be carried via an inert gas into a spectrophotometer for measurement. SRNL scientists theorized that the addition of stannous chloride to the groundwater passing through the air stripper should enable mercury to volatilize and be removed in the stripper. Laboratory tests were successful, so a full-scale system was placed into operation in December 2007. The full-scale process was also successful, removing mercury in accordance with the following reaction.

$HgCl^0 + Sn^{+2} = Hg^0 + 2Cl^- + Sn^{+4}$

Since tin is a significant component in stannous chloride, it was necessary to maintain the concentration of this compound at a minimum in order to protect the receiving stream. SCDHEC issued a permit to construct the treatment system on the basis that the stannous chloride concentration in the effluent would not exceed the minimum toxicological value found in the Environmental Protection Agency's ECOTOX database. After adjusting the lethal concentration at which fifty percent of the laboratory test organisms (*Daphnia magna*) died (LC50 = 13,500 ug/l) with a safety factor of 33 (taken from SCDHEC regulation 61-68), this value was determined to be 409 ug/l – well above the stannous chloride concentration necessary to enable mercury volatilization.

Humic Acid Addition for Outfall with Low Metal Concentrations

SRS personnel struggled to find the lowest cost method for removing copper and zinc from this outfall. It has highly variable flows and relatively low pollutant concentrations. Figure 3 shows typical concentrations of copper versus the future limits, while Figure 4 shows typical daily flow fluctuations.

Figure 3. Outfall copper concentrations versus future limits

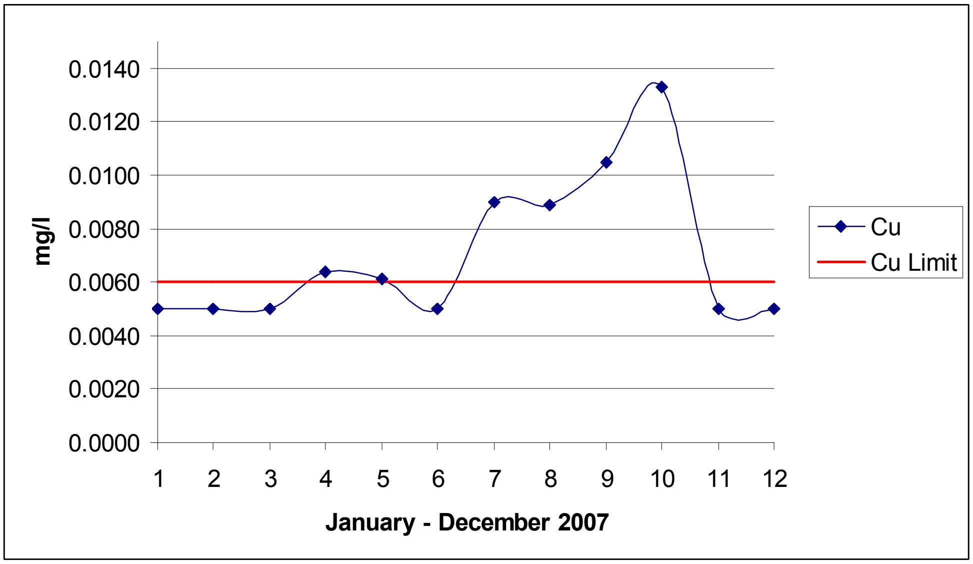
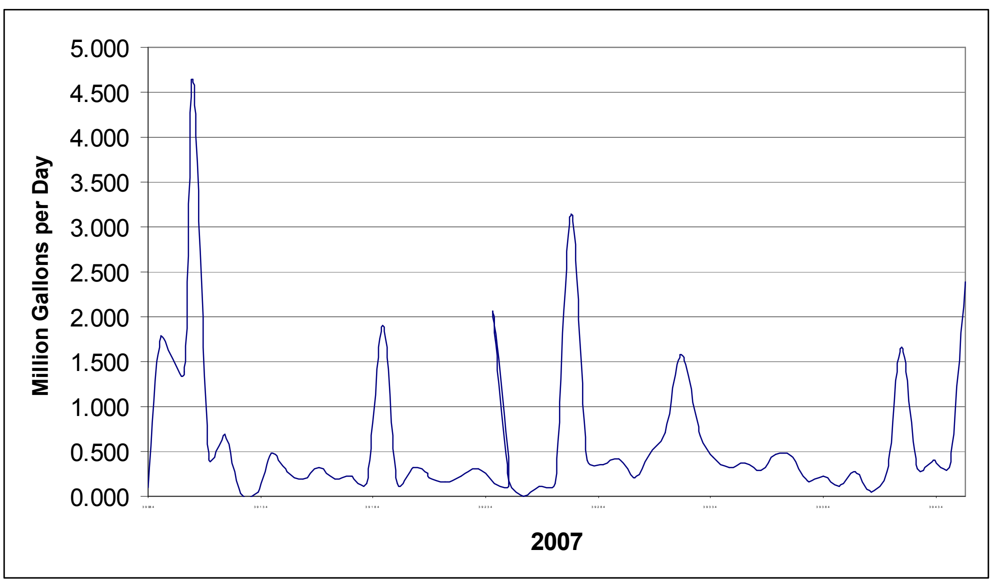
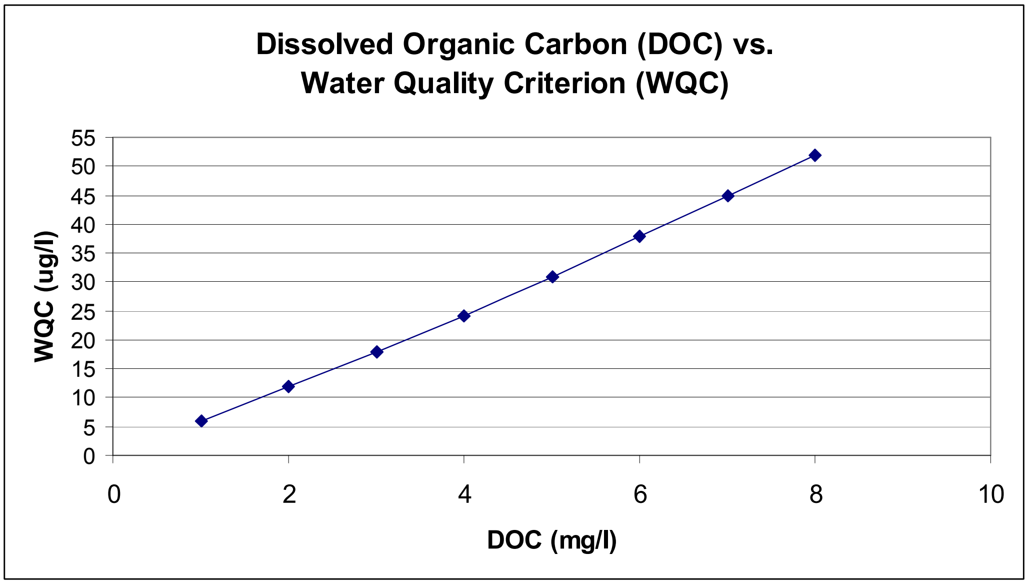


Figure 4. Typical outfall daily flow fluctuations



Treatment options such as ion exchange and constructed wetlands were considered. Capital and operating costs were excessive for ion exchange and there was not enough land available to construct wetlands. A constructed peat bed was given careful consideration, but was eventually abandoned due to cost. In February 2007, USEPA published their final biotic ligand model (BLM) for copper. Calculated using the BLM, Figure 5 shows the impact of higher effluent dissolved organic carbon (DOC) concentrations on copper water quality criteria.

Figure 5. DOC impact on copper water quality criteria



SRS personnel wanted to take advantage of this option to raise the copper limit, but the DOC concentration in the outfall effluent was too low for the BLM to help. While conducting a literature search, it became apparent that DOC is available commercially as humic acid. This product is normally used for agricultural purposes; however, SRS personnel theorized it could be used as an outfall additive to raise the effluent DOC concentration and enable calculation of higher copper limits via the BLM.

Data needed to run the BLM was collected on the outfall discharge. It was also collected on the receiving stream. Receiving stream data was needed in order to ensure that the amount of DOC required at the outfall would not raise the naturally occurring stream DOC concentration, possibly altering indigenous macroinvertebrate populations. BLM calculations were completed at varying pH and DOC concentrations since the model is most sensitive to these parameters. The results were provided to SCDHEC along with a request to construct a chemical feed facility to add humic acid to the outfall effluent. SCDHEC approved the request under the conditions that (1) DOC would not be added at a concentration that would raise the naturally occurring stream concentration, and (2) that antibacksliding provisions of the regulations would be met (the copper limit could not be raised above the existing limit of 25 ug/l). SRS personnel proceeded with design of the chemical feed system and hired a contractor to construct it early in 2009.

EPAs BLM is available for copper but not other metals, such as zinc. Although data indicated that the new zinc limit at this outfall would probably be attained most of the time, the risk of noncompliance was great enough to require action. One scientific option that is available to NPDES permittees is the Recalculation Procedure (RP). In essence, the RP develops site-specific water quality criteria based upon a comparison of the receiving stream’s actual biological community to the biological community that was assumed when national criteria were developed. When some of the more sensitive species are not present in the receiving stream, they are replaced with species that are present. In many cases, higher water quality criteria may be calculated. For this outfall, a subcontractor was hired to perform a biological assessment of the receiving stream and develop a site-specific zinc standard.

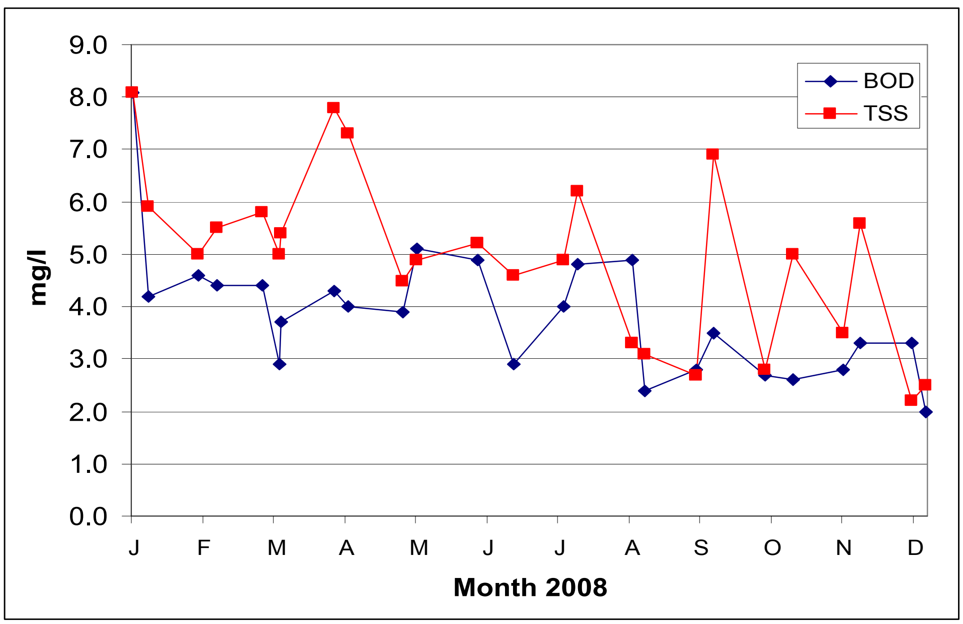
RESULTS

All of the innovative compliance alternatives were installed in time to meet compliance deadlines and each has operated successfully. All outfalls continue to comply with NPDES permit limits. Several million dollars were saved by not installing and operating conventional treatment systems. Key results are explained in the following sections.

Treatment of Clean Water in CSWTF

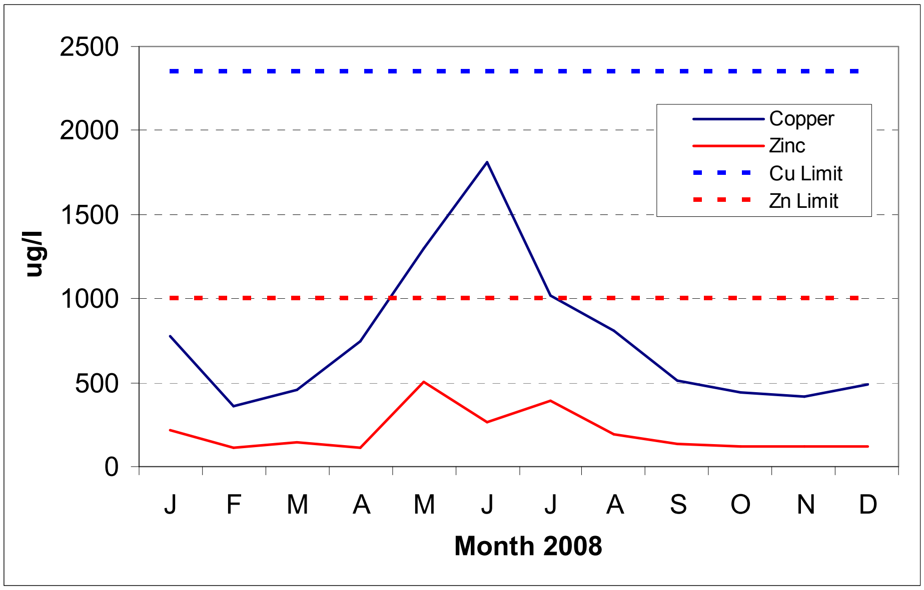
All outfalls discharging low volumes of relatively clean water had been connected to the CSWTF collection system by the end of 2007. As predicted by the full-scale study, the addition of this water did not cause any operational problems for the treatment plant. Figure 6 provides effluent Biochemical Oxygen Demand (BOD) and Total Suspended Solids (TSS) data for 2008. All data are well below permit limits.

Figure 6. CSWTF effluent BOD and TSS data after addition of clean water



Personnel who operate the CSWTF ensure that the clean water sources they receive for treatment remain within acceptable volume and concentration limitations. In order to do so, they require periodic analyses (Figure 7). If metals concentrations increase, dischargers are required to take action before problems arise at the CSWTF.

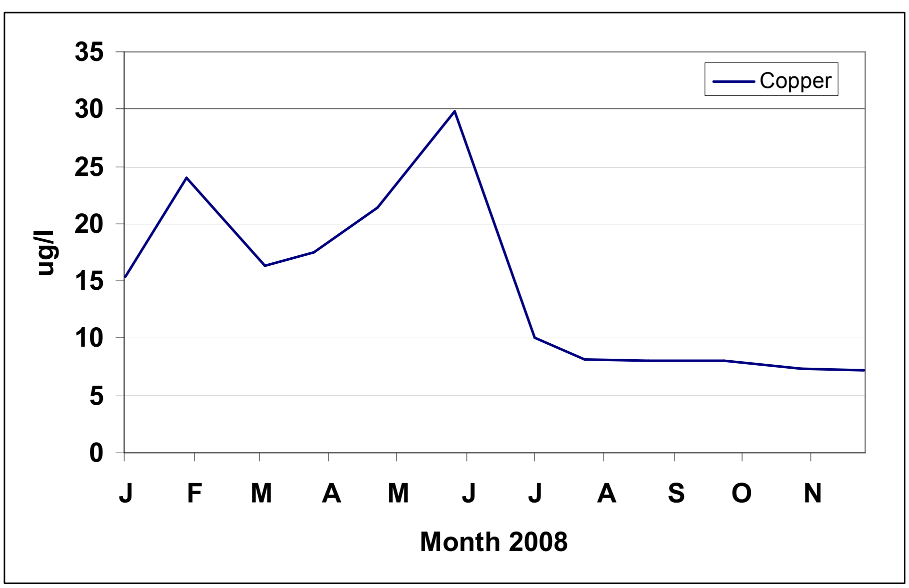
Figure 7. "Worst case" metals data from one clean water source



Wetlands Treatment

The treatment wetland required several months for plants to develop well enough to provide adequate copper removal. Plant growth was minimal at first and additional plants were added to decrease the amount of time needed to provide coverage throughout the treatment basins. Before plants were well established, algae were problematic. Once plants began to proliferate, the algae problem subsided and copper removal improved greatly. As indicated in figure 8, the summer growing season provided a quick transition to the wetland's ability to remove copper.

Figure 8. Copper removal by constructed wetland wastewater treatment plant

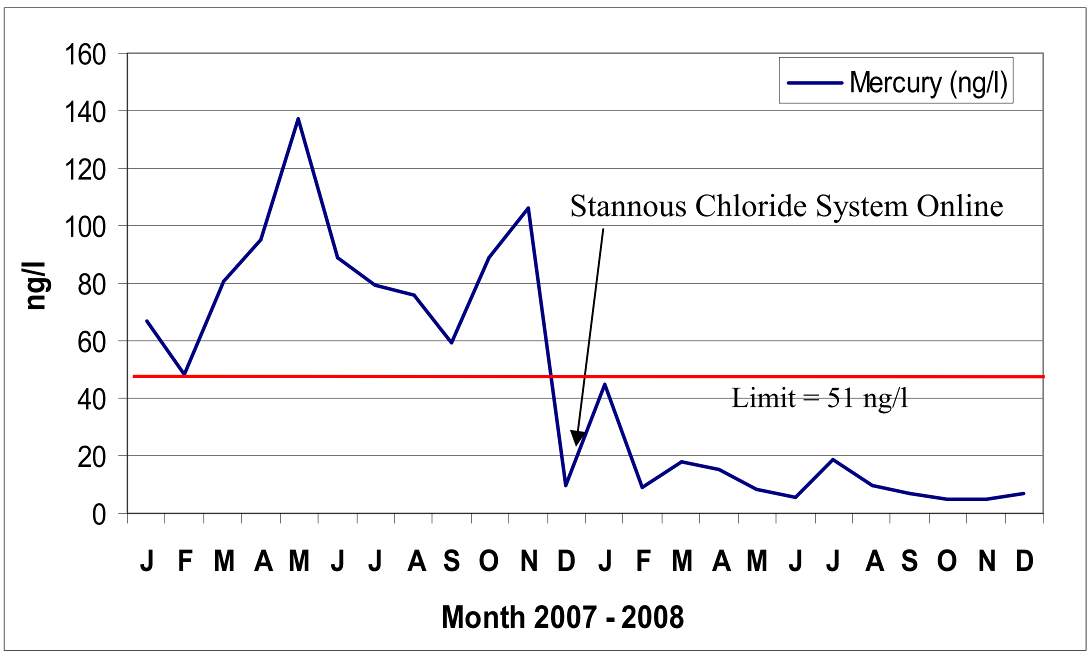


Although the average copper concentration in the wetland declined to 8 ug/l during the latter half of 2008, the average permit limit of 7 ug/l would have been in jeopardy had a WER not been completed on the wetland effluent. The WER resulted in enabling SCDHEC to raise the average copper limit to 32 ug/l. Thus, the original plan to construct a treatment wetland and complete a WER on its effluent was successful in providing a long-term solution to the copper problem at this NPDES outfall.

Stannous Chloride Treatment

Only a small volume of stannous chloride is needed in order to volatilize mercury for removal in the air stripper. Therefore, the system that was constructed to accomplish this task was small enough to fit in a cabinet located near the stripper. Construction costs were minimal. At a feed rate of only a few liters per day, the cost to operate the system is also minimal. Thus far, the mercury permit limit of 51 ng/l has been attained easily (Figure 9).

Figure 9. Mercury removal by stannous chloride treatment system



Since mercury removal must be provided whenever the air stripper is online, and since the stripper runs seven days per week, twenty-four hours per day, it is critical that it operate properly. Instrumentation is provided to notify certified operators of problems with the stannous chloride feed system. Operators have learned that it is critical to select high quality peristaltic pumps and tubing for this system.

Humic Acid Addition

At the time this paper was written, the Humic Acid Addition System had only been operational for two weeks and new permit limits had not yet gone into effect. However, the system was operating well and had experienced only minor glitches. All indications are that it will enable compliance with the NPDES permit. Although normally translucent effluent had become amber in color due to the addition of humic acid, this is not problematic since it enters a black water receiving stream. A picture of the Humic Acid Addition System is shown in Figure 10.

Figure 10. Humic Acid Addition System

DISCUSSION

In recent years, changes in the way water quality standards are converted into NPDES permit limits for hardness-dependent metals such as copper, lead and zinc have resulted in the need for creative compliance solutions. Rather than basing limits on a default stream hardness of fifty milligrams per liter, Regulators are basing them upon the measured stream hardness. In addition, laboratory detection capabilities have improved to the point where metals may be measured at very low concentrations. For permittees who discharge into low-flow receiving streams, these factors are resulting in extremely low metals limits.

After issuance of a new NPDES permit in 2003, SRS was faced with very low metals limits at several outalls. The cost to comply was estimated to be over $25,000,000. These expenses would have been incurred at a time when the SRS budget was declining annually. The compliance options selected for implementation and described herein saved SRS several million dollars.

In order to take advantage of these creative options, it was important that the regulating authority (in this case SCDHEC) be open-minded and flexible. Mercury removal by air stripping required the addition of stannous chloride. Compliance with copper limits required the addition of humic acid in conjunction with biotic ligand modeling. Compliance with zinc limits required completion of a Recalculation Procedure. Large volumes of clean water were being treated within a biological treatment system that might not function properly if the influent wastewater was too dilute. These unique ideas required that SRS personnel work closely with SCDHEC to help ensure success.

As is often the case with new ideas, these projects experienced some problems. For example, the constructed wetland treatment system developed algae that caused pH problems. Algae were difficult to eliminate since many of the options that would eradicate them might adversely impact the wetland. The use of most pesticides was out of the question. An ultrasonic system was tested, but it destroyed only certain species of algae. Ultimately, as the wetland developed, shading from normal plant growth eliminated the algae problem. In another example, the feed rate on the stannous chloride addition system had to be watched carefully after startup in order to ensure that mercury was removed adequately. Minor problems with the pump and tubing also had to be addressed.

Since the algorithm that was developed to control the feed rate of chemical from the Humic Acid Addition System is impacted greatly by pH, it became apparent that it was very important to maintain effluent pH as close to neutral as possible. Low outfall pH values would result in higher feed rates, thus increasing operational costs. Activities that helped control effluent pH required operational adjustments that increased work activities slightly, but were not expensive.

CONCLUSIONS

There are several conclusions that may be drawn and lessons that may be learned from the work undertaken to meet stringent effluent metals limits, as outlined below.

- Due to improvements in laboratory techniques and tightening of water quality standards, NPDES permit limits for hardness dependent metals are declining. Many permit holders are being faced with increased expenses to comply.
- Constructed wetlands alone may not be capable of meeting very low metals limits; however, their effluents are typically non-toxic and should enable development of a successful WER. The combination of wetlands treatment with completion of a WER can make compliance possible.
- Where the costs to remove hardness-dependent metals from a discharge are prohibitive, it may be possible to add humic acid and complete a biotic ligand model to have limits raised, enabling compliance in a more cost effective manner. Considering the fact that storm water regulations are becoming more stringent, humic acid addition could also be considered as a possible storm water best management practice (BMP), under the right circumstances.
- Wastewater with essentially no biochemical oxygen demand that contains low metals concentrations can be considered for treatment in a biological treatment system, as long as adequate testing is performed beforehand.
- Tin chloride may be injected into wastewater contaminated with low levels of divalent mercury, enabling mercury to be removed through some form of air sparging.
- It is important to work closely with regulatory authorities on unique compliance ideas in order to ensure successful implementation.

- Under the right circumstances, it is possible to achieve considerable cost savings from the use of unique treatment systems instead of conventional treatment options.

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