

# DETOXIFICATION OF OUTFALL WATER USING NATURAL ORGANIC MATTER

Nancy Halverson, Brian Looney, Margaret Millings, Ralph Nichols, Jay Noonkester, William Payne

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AUTHORS: Nancy Halverson, Brian Looney, Margaret Millings, Ralph Nichols, Jay Noonkester, Building 773-42A, Savannah River National Laboratory, Aiken, SC 29808

William Payne, Building 705-3C, Savannah River Nuclear Solutions, Aiken, SC 29808

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**Abstract.** To protect organisms in an ephemeral stream at the Savannah River Site, a proposed National Pollutant Discharge Elimination System permit reduced the copper limit from 25 µg/L to 6 µg/L at Outfall H-12. Efforts to reduce copper in the wastewater and stormwater draining to this outfall did not succeed in bringing copper levels below this limit. Numerous treatment methods were considered, including traditional methods such as ion exchange and natural treatment alternatives such as constructed wetlands and peat beds, all of which act to remove copper. However, the very low target metal concentration and highly variable outfall conditions presented a significant challenge for these treatment technologies. In addition, costs and energy use for most of these alternatives were high and secondary wastes would be generated.

The Savannah River National Laboratory developed an entirely new “detoxification” approach to treat the outfall water. This simple, lower-cost detoxification system amends outfall water with natural organic matter to bind up to 25 µg/L copper rather than remove it, thereby mitigating its toxicity and protecting the sensitive species in the ecosystem. The amendments are Organic Materials Review Institute certified commercial products that are naturally rich in humic acids and are commonly used in organic farming.

## INTRODUCTION

A National Pollutant Discharge Elimination System (NPDES) Permit was issued to the Savannah River Site (SRS) by the South Carolina Department of Health and Environmental Control (SCDHEC) and became effective on December 1, 2003. The new permit reduced the copper limit from 25 µg/L to 6 µg/L at Outfall H-12, with a compliance date of July 1, 2009. Sources of copper to the outfall were identified and potential process modifications (feedwater changes, chemical changes, operational changes, etc.) were considered and tested. These efforts to reduce copper in the wastewater and stormwater draining to the outfall did not succeed in bringing copper levels

below the proposed limit. SRS management decided to install a new type of treatment system at the outfall.

## BACKGROUND

Outfall H-12 is located in the center of SRS in Aiken, SC. The outfall collects nonprocess cooling water, cooling tower and air compressor blowdown, steam condensate, radiological control retention basin water, well water flushes and overflow, and stormwater. The outfall discharges to an ephemeral tributary of Fourmile Branch, which drains to the Savannah River. Copper generally ranges from <5 µg/L to 13 µg/L at the outfall.

The major sources of wastewater to Outfall H-12 are batch releases from various operating facilities, including:

- A cooling water delaying basin, that releases 187,000 gallon (708 m<sup>3</sup>) batches, 2 – 3 times per day at approximately 6,200 gpm (23 m<sup>3</sup>/min).
- A 6.85 million gallon (65,900 m<sup>3</sup>) detention basin that is released as needed at 350 or 700 gpm (1.3 or 2.6 m<sup>3</sup>/min).
- A 2.7 million gallon (10,000 m<sup>3</sup>) detention basin that is released as needed at 350 or 700 gpm (1.3 or 2.6 m<sup>3</sup>/min).
- Occasional production well flushes at approximately 1,000 gpm (4 m<sup>3</sup>/min) (U.S. DOE, 2008).

Stormwater from 193 acres in the center of SRS also drains to Outfall H-12. The 25-year, 24-hour storm event was estimated to create a total runoff volume of 19.7 million gallons (WSRC, 2007). The maximum process and stormwater flow to Outfall H-12 was estimated to be 1,571,000 gpd (5946 m<sup>3</sup>/day) (WSRC, 2008).

Copper is found in both the process water and stormwater discharges. Process water originates from various production wells pulling water from the Crouch Branch and McQueen Branch aquifers, which contain natural low levels of metals, including copper. The well water contains significant levels of copper during initial pump startup due to either natural metal concentrations in

groundwater or bronze components in the production wells. Other sources of copper include copper tubing and fittings in the operating facilities, picked up by stormwater flowing over equipment and paved areas.

## EXPERIMENTAL DESIGN

### Consideration of Alternatives

Numerous alternatives were evaluated for treatment of H-12 wastewater. These alternatives included three primary treatment technologies — ion exchange, wetlands, and peat bed treatment, all of which act to remove copper from the wastewater. However, the very low target metal concentration and highly variable outfall conditions (flows ranging from zero to over 8,000 gpm and pH ranging from 4.8 to 8.5) presented a significant challenge for the treatment technologies. In addition, costs (>\$10 million) and energy use for most of these alternatives were high, secondary wastes would be generated, and in the case of wetland treatment, sufficient land was not available near the industrial facilities.

Water management alternatives that did not include treatment were also evaluated, including direct discharge to a larger stream, injection wells, process water discharge reduction, and renegotiation of discharge limits. These options were rejected for various reasons including cost, the need for a backup solution, and engineering determinations that certain alternatives would not solve the problem.

### New Approach

To resolve the issue, the Savannah River National Laboratory (SRNL) developed an entirely new “detoxification” approach to treat the outfall water. This simple, lower-cost (approximately \$2 million) detoxification system amends outfall water with natural organic matter to bind up to 25 µg/L copper rather than removing copper to meet the new, very low, 6 µg/L limit. The new approach mitigates the copper’s toxicity and protects the sensitive species in the ecosystem.

The detoxification process was made possible when the EPA published their Biotic Ligand Model (BLM) in 2007 (EPA, 2007c). The BLM calculates copper toxicity based on water quality parameters such as pH, dissolved organic carbon (DOC), and percentage of the DOC that is contributed by humic acid. The BLM predicts how DOC in the water binds with copper in the water, limiting the availability of copper to interact with “biotic ligands,” such as gill membranes, thus reducing impacts to aquatic organisms such as the *Daphnia* (“water flea”) and resulting in water chemistry that more closely mimics natural streams.

SRNL used the EPA’s Biotic Ligand Model Windows Interface, version 2.2.1, by HydroQual, Inc., to calculate

predicted copper toxicity to aquatic organisms (EPA 2007, a,b). The baseline BLM runs were performed by setting the pH, alkalinity and other parameters to cover the expected range of those parameters at the outfall. The modeling results confirmed that an addition of DOC in concentrations similar to the receiving stream could reduce copper toxicity in the outfall water (Millings et al., 2008a), allowing the goal of the proposed NPDES permit to be met even if copper is present at concentrations greater than 6 µg/L.

Since Outfall H-12 had been able to meet the older copper limit of 25 µg/L, the goal set for the DOC addition system was to detoxify copper up to this concentration. BLM results showed that, for humate amendments, DOC values of approximately 22 mg/L or less would render 25 µg/L copper non-toxic at all outfall pH values  $\geq 5.9$  (Millings et al., 2008b). Higher pHs required less DOC addition.

SRNL tested seven organic carbon amendment products to determine the best candidates. These amendments are OMRI (Organic Materials Review Institute) certified commercial products that are high in humic compounds or similar molecules and are typically used as soil additives in organic farming. The amendment chosen was a commercial potassium humate product made by extracting the raw material with a potassium hydroxide base solution. The high pH dissolves the humic acid molecules and generates a dark-brown stock solution with pH greater than 7.

### Process Control Equation

The BLM calculations provided the foundation for developing a process control equation for addition of humate to the outfall. The control system theory is depicted graphically in Figure 1. A sensitivity analysis indicated that the BLM model was strongly dominated by

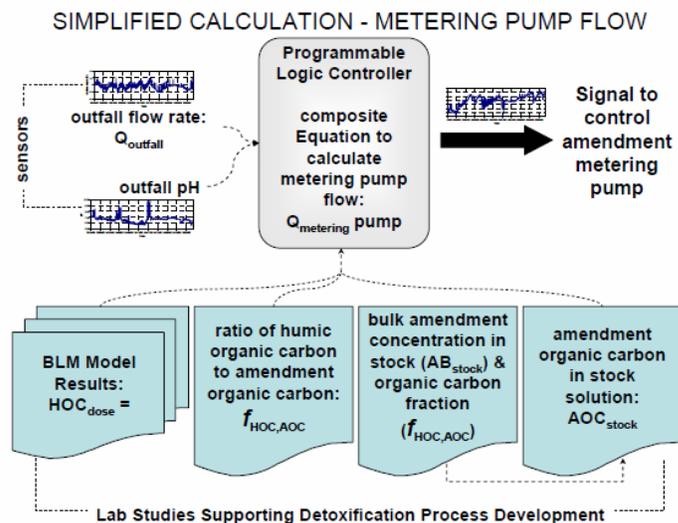


Figure 1. Copper detoxification control theory.

DOC and pH (Millings et al., 2008b). Thus, calculation of the required concentration of DOC at any point in time to achieve a specified toxicity level is primarily a function of outfall pH and flow. The entire equation-development sequence included: 1) determining target humic organic carbon (HOC) concentrations using the BLM, 2) developing a simplified mathematical relationship between HOC and pH, 3) determining the humic acid content and HOC content of the amendment, and 4) combining all of this information into an overall process control equation. Consistent with this control theory, the specific process control equation developed for use by the programmable logic controller (PLC) to add humate amendment to mitigate copper toxicity in the H-12 Outfall is presented below:

$$Q_{\text{metering pump}} = Q_{\text{outfall}} \times$$

$$\left[ \frac{(9.465 \times 10^{11})(10^{-\text{pH}})^2 + (1.690 \times 10^7)(10^{-\text{pH}}) + 1.108}{AB_{\text{stock}} f_{\text{AOC,AB}} f_{\text{HOC,AOC}}} \right]$$

where:

$Q_{\text{metering pump}}$  is the required flow of bulk amendment to treat the outfall.

$Q_{\text{outfall}}$  is the flow of water at the outfall.

$AB_{\text{stock}}$  is the bulk amendment concentration in the stock solution, or mg bulk amendment/L of solution.

$f_{\text{AOC,AB}}$  is the ratio of mass of total organic carbon in the bulk amendment to the mass of the bulk amendment, as determined in the laboratory.

$f_{\text{HOC,AOC}}$  is the ratio of the mass of humic organic carbon in the amendment to the mass of total organic carbon in the amendment, as determined in the laboratory (Looney and Millings, 2009).

### Humate Addition System

A humate addition system was designed to treat an average daily outfall flow rate of 700 gpm (2.6 m<sup>3</sup>/min), with a range up to 8,000 gpm (30 m<sup>3</sup>/min) [the maximum process flow of 7,000 gpm (26 m<sup>3</sup>/min) plus a potential simultaneous discharge of 1,000 gpm (4 m<sup>3</sup>/min) of well flush water] (U.S. DOE, 2008). Flow rates above 8,000 gpm (30 m<sup>3</sup>/min) were attributable to stormwater, which is not required to be treated, so the system was not designed to “treat” the portion of flow in excess of 8,000 gpm (30 m<sup>3</sup>/min).

The system consists of two double-walled 5,500 gallon (21 m<sup>3</sup>) storage tanks, each with a level transmitter, annular-space leak detection system, and recirculation pump to keep the potassium humate in suspension (Figure 2). A small flow of domestic water acts as a carrier solution to prevent settling of the potassium humate



Figure 2. Humate addition system.

solution in the piping when demand is low. Two metering pumps, cross connected to the two tanks to provide backup capability, are controlled by a PLC. Flow meters in the two contributing industrial wastewater streams and a pH meter at the outfall feed data to the PLC to calculate and deliver the appropriate dose of amendment using the process control equation. Duplicate flow and pH meters provide backup capability.

### CONCLUSIONS

The publishing of the EPA’s BLM paved the way for a new technique for solving a difficult copper compliance problem at Outfall H-12. A detoxification system was developed which measures the pH and flow of the outfall’s component streams, calculates the amount of DOC needed to detoxify the outfall water using the BLM, and calculates and delivers the appropriate dose of a humate additive to the outfall. The detoxification system, which began operating in June 2009, protects and improves the environment by reducing the copper’s toxicity rather than removing copper. In comparison with the other treatment alternatives considered, the detoxification system resulted in reduced energy use, land disturbance, and costs, and eliminated generation of secondary waste. SCDHEC approved the system and allowed the outfall to maintain its 25 µg/L copper limit rather than implementing a new 6 µg/L limit.

An application for a process patent was filed with the U.S. Patent and Trademark Office in January 2009. This will make the technology available to others for use at appropriate sites.

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