# Report as of FY2007 for 2005NC44B: "Use of Indicators to Distinguish Between Point and Non-Point Sources of Chemical Contamination in North Carolina Streams"

# **Publications**

Project 2005NC44B has resulted in no reported publications as of FY2007.

# **Report Follows**

# Title

Use of Indicators to Distinguish Between Point and Non-Point Sources of Chemical Contamination in North Carolina Streams

# **Project Summary**

Effluent discharged into receiving streams from wastewater treatment plants has to meet National Pollutant Discharge Elimination System permit levels on a variety of parameters that are designed to protect the stream's ecology and aquatic life from deleterious effects and to ensure that the natural flora and fauna can remediate the residual chemicals and micro-organisms prior to subsequent usage. As new chemicals are constantly being introduced into the domestic and industrial market, it is inevitable that they will be found in the raw waters entering these treatment plants. When their presence in receiving streams is undesirable, research studies are implemented to evaluate alternate approaches to control their levels in plant effluents. No equivalent gesture is guaranteed for the same fate of these chemicals originating from nonpoint sources. Consequently, downstream reservoirs and lakes are likely to be sinks for many of these compounds from a variety of unregulated sources. The management of nonpoint source contamination wasn't designed to account for the presence of chemicals with far different properties to those mimicking natural compounds and the presence of pharmaceutically and endocrine active chemicals with biological functions in environmental waters is testament to the ineffectiveness of current contaminant control. Drugs used for human and animal therapy and endocrine-disrupting compounds are introduced into agricultural systems via land application of recycled wastewater and accumulated biosolids as well as through direct usage of pesticides. The widespread domestic use of many of these compounds also ensures that they will be present in septic systems and in landfills. Leakage and runoff from any of these systems will contribute significant loading into receiving waters and contribute to impairment. It is unknown what percentage of accumulations of these compounds derive from point and non-point sources but from extrapolation of what is known about nonpoint pollution from regulated compounds, the contribution from the nonpoint sources is likely to be very significant.

Until now, it has been a major challenge to provide an effective strategy that would permit identification of non-point sources of chemical pollution as distinct from point sources. This proposal will investigate the use of chemical profiling that distinguishes between point and non-point sources of pollution and develop an approach for characterizing the contributions of surrogate measures of chemical contamination in the form of antibiotics and endocrine disrupting hormones and pesticides from land application runoff and on-site wastewater treatment seepage. The results of this study will provide an indication of the relative contributions to overall pollution from chemicals originating in both point and non-point sources and a strategy that can be applied to survey impaired streams for these chemicals.

### Methodology

During the first 6 months of this project we have reviewed the literature to assist in making reasoned judgments about the identity of chemicals that will serve as indicators to distinguish between point and nonpoint sources of surface water contamination. For conventional wastewater treatment plants that use chlorine for final disinfection we are targeting the nonvolatile haloacetic acids that we have detected in the effluents of several plants across North Carolina practicing effective nitrification. We have adapted standard methods for these analyses usually deployed for levels in excess of I pg/L in finished drinking waters so that we can monitor their fate downstream of the point of discharge at levels as low as 20ng/L. Chlorinated haloacetic acids (HAAS) are proposed as an indicator of wastewater treatment plant effluent in surface waters with the hypothesis that they will be created as the wastewater is chlorinated before discharge and will not be 1.en1oved during dechlorination. It is also hypothesized that H.4.4~ will

not be created in septic system treatment since. in normal household use, there will be insufficient dose to create them.

Wastewater treatment plant (WWTP) effluent samples have been collected from Morgan Creek and sampled were collected upstream of the effluent discharge. approximately 10 feet below the discharge point, and at approximately **0.5** miles downstream of the discharge point. This wastewater treatment plant is chlorinated with sodium hypochlorite, which is delivered usually in a 15% solution. The dose rate varies daily, but an average dose rate is 2.5 mg/L. Upstream samples contained no measurable HAAs and there are no documented upstream wastewater plant discharges. Samples at both points in the receiving creek after discharge from the Orange Water and Sewer Authority WWTP do contain measurable levels of both dichloroacetic acid (Cl<sub>2</sub>AA) and trichloroacetic acid (Cl<sub>3</sub>AA). The levels are somewhat lower than would be expected with the chlorine dose and contact time employed. This is likely due to incomplete nitrification of the effluent prior to chlorination and measurable levels of ammonia that would have been converted to chloramines and, therefore, unavailable for the formation of high levels of HAAs. Nevertheless, in order to use HAAs as a tracer of chlorinated wastewater it became apparent that the analytical method will have to be evolved to target lower concentrations. Method development for this is almost complete and involves either solid phase extraction of acidified 200mL filtered aqueous samples into 1mL extracts or the blowing down to 200µL of liquid-liquid solvent extracts prior to derivatization. The target quantitation limit is 20ng/L and we are currently able to reproduce measurements at 50ng/L spiked into the upstream Creek samples. We are currently studying the occurrence fate and transport of HAAs discharged from the City of Burlington South plant that practices both nitrification and chlorination.

Septic effluent sample collection locations were established with the assistance of Mr. Steven Berkowitz of NC DENR. Samples were collected during state inspections of systems with sand filters. At the time of sample collection, the systems were in operation and samples were collected as effluent trickled into the ranks. Samples were also collected from a failed septic system after digging up the drainage trench with a backhoe. Visibly there **was** effluent on the ground surface and flowing straight from the trench. Additional samples were collected from a septic system associated with an office building with the design created by Integrated Water Systems Inc. with who we have established collaboration on this project. A schematic showing the various unit processes employed with this system and the sample points from which samples were collected is shown in Figure 1.

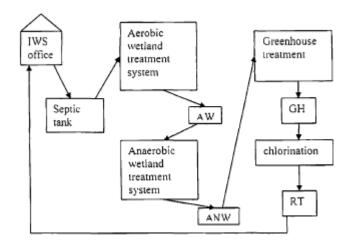


Figure 1. Integrated Water Systems Office (Chatham County) Septic System Design (AW, ANW, GH, RT are the sampling locations)

Flow was turned on and samples were collected starting six minutes later as effluent began to move through the system. Samples were collected from the septic tank (ST), after aerobic wetland treatment (AW), after anaerobic wetland treatment (ANW), after greenhouse treatment (GH), and from the chlorinated reuse tank (RT). ST and RT were collected by dipping the sampling cup into liquid collected at bottom of tank. AW, ANW, and GH samples were collected by filling the sampling cup from the flow and pouring this into 40mL vials with preservation agent. The sampling cup was rinsed with laboratory-grade water (LGW) between sampling locations. The effluent in the greenhouse tank (GH) is exposed to chlorination fumes from the reuse tank. Free chlorine measurements were collected onsite with a HACH colorimeter using each sample as its own blank. Levels were determined at ST, AW, ANW, GH, and RT as 0, 0.09, 0.03, 0.16, and 2.2 mg/L respectively. Haloacetic acid concentrations were below detection in the samples collected before exposure lo chlorine (i.e. AW, ANW, and GH) but were at concentrations above the highest calibration curve level of 50 pg/L in the samples collected from the reuse tank. However, the samples collected prior to chlorination would be more typical of domestic use of septic systems and the non-detectable HAAs were consistent with the non-detects in the other septic systems sampled. We can conclude, therefore, that haloacetic acids are unlikely to be found in septic systems.

Tracers for septic systems are also being evaluated. Triclosan and caffeine are the chemicals chosen for this study based on a review of previous research reports that includes occurrence data for these chemicals in a variety of conventional wastewater treatment plant effluents. Methods have been adapted for the analysis of these chemicals in the aqueous phases of septic system waste down to concentrations of 20 ng/L The systems sampled for HAAs described above were also analyzed for both caffeine and triclosan. Levels up to  $1 \mu \text{g/L}$  of caffeine were detected in the samples collected from the drainage ditch and we are currently evaluating the transport of this tracer as h e septage moves through the topsoil towards a nearby receiving stream.

#### **Principle Findings**

This study has been looking at two major sources of nonpoint contamination of surface waters; failed septic systems and land application of biosolids. Caffeine and triclosan were proposed as indicators of nonpoint sources of pollution originating from failed septic systems due to their elevated levels in septic tanks compared to effluents from wastewater treatment plants (WWTPs). Caffeine from WWTP effluents (n-29) ranged below detection (BD) to 1.2µg/L. Both analyses were detected in pooled sewage around failed systems (n=3) at average concentrations of 2.3µg/L caffeine and 1.6µg/L triclosan. Caffeine was detected downstream of a failed septic system during a rain event an average of 270ng/L. The results indicate that these compounds survive in septage that has surfaced and have the possibility to flow overland to streams.

The combination of aerobic and anaerobic degradation processes used in advanced treatment with septic tanks reduce the high concentrations in the septic tank (average caffeine (n-7):  $26\mu g/L$  and triclosan (n-7):  $1.5\mu g/L$ ) to an average of 70ng/L for both compounds after treatment. Advanced treatment systems using these processes are effective at removing these indicator compounds and these results can be extrapolated to suggested that a functioning septic system would also effectively remove them.

The potential for biosolids to pollute surface water, particularly with endocrine disrupting chemicals has been demonstrated in this research. The biosolids assessed in this study were from two separate wastewater treatment plants, one of a large city (Plant B) and the other of a small town (Plant A). Surprisingly, the

concentrations of nonylphenols and triclosan due to were less in the larger city. Upon review of different methods of treatment at the wastewater plants, it seemed possible that the Plant B biosolids had lower concentrations of nonylphenols and triclosan due to the shorter solids retention time (SRT) and a more aerated process for conditioning the biosolids. This suggested that wastewater treatment plants with a shorter SRT would accumulate less contaminants, although this could cause greater concentrations in the wastewater effluent. The aeration of the biosolids that occurs during limekiln treatment may also assist in the degradation of nonylphenols, which is mainly by aerobic organisms. There is also concern that these contaminants will cycle from a domestic waste stream back into drinking water through contamination of the source water used to produce drinking water. This further promotes the need to remove these contaminants from biosolids as an action to prevent their contamination in surface water. Triclosan may be degraded through photolysis and nonylphenols through microbial degradation, which could be incorporated into the processes for drinking water treatment.

### Significance

The potential for biosolids to pollute surface water, particularly with endocrine disrupting chemicals has been demonstrated in this research. The biosolids assessed in this study were from two separate wastewater treatment plants, one of a large city (Plant B) and the other of a small town (Plant A). Surprisingly, the concentrations of nonylphenols and triclosan due to were less in the larger city. Upon review of different methods of treatment at the wastewater plants, it seemed possible that the Plant B biosolids had lower concentrations of nonylphenols and triclosan due to the shorter solids retention time (SRT) and a more aerated process for conditioning the biosolids. This suggested that wastewater treatment plants with a shorter SRT would accumulate less contaminants, although this could cause greater concentrations in the wastewater effluent. The aeration of the biosolids that occurs during limekiln treatment may also assist in the degradation of nonylphenols, which is mainly by aerobic organisms. There is also concern that these contaminants will cycle from a domestic waste stream back into drinking water through contamination of the source water used to produce drinking water. This further promotes the need to remove these contaminants from biosolids as an action to prevent their contamination in surface water. Triclosan may be degraded through photolysis and nonylphenols through microbial degradation, which could be incorporated into the processes for drinking water treatment.

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