

Report for 2003MD28B: Fate of Alkylphenolic Compounds in Wastewater Treatment

There are no reported publications resulting from this project.

Report Follows

Yearly project report March 2003 - February 2004

Fate of alkylphenolic compounds in wastewater treatment plants and a sub-estuary of the Chesapeake Bay

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Statement of Problem and Research Objectives

Recently, a series of studies have raised concerns about the presence of persistent organic pollutants in natural waters and the capability of wastewater treatment plants (WWTPs) to remove such chemicals from their effluents. The last decade has also seen an increased interest in pollutants suspected to interfere with the endocrine system, commonly referred to as endocrine disrupters. One such compound is 4-nonylphenol (NP), which was found to produce the same effects as estradiol in a line of cancer cells (Soto et al. 1991). NP is a precursor in the synthesis of the nonylphenol ethoxylates (NPnEOs), one class of alkylphenol ethoxylates (APnEOs). APnEOs are nonionic surfactants that have been widely used in industrial processes and as detergents in both industrial and household applications for more than thirty years. After being used, the APnEOs are discharged into wastewater and are treated in WWTPs. During wastewater treatment, APnEOs are subject to microbial degradation processes that produce different metabolites (NP among them), which are ultimately released into natural waters. The APnEOs have been signaled as a current pollution issue in the Chesapeake Bay and were highlighted in a recent workshop on emerging contaminants organized by the Scientific and Technical Advisory Committee of the Chesapeake Bay Program on October 18, 2002 at Solomons Island. Currently, little information exists on the presence of these compounds in the State of Maryland or the Chesapeake Bay itself. The main objective of the proposed work is to model the distribution and fate of APnEOs and their degradates (APs) in a sub-estuary of the Chesapeake Bay and a WWTP and, at the extent possible, determine how operating parameters at the plants control the concentrations of these endocrine-active substances in the estuary.

Methodology

A main limitation for their study is the limitation of analytical techniques for their analysis in natural waters. As part of this project we proposed to develop a protocol for the sampling and analysis of NPnEOs and OPnEOs and their derivatives in effluent and natural samples. We also proposed the development of a “Mass Balance and Distribution” model.

Principal Findings

During the first year of the project, we have focused our work in the development of the required analytical methods, and we have initiated the development of the theoretical model.

Analytical method development

As stated in the proposal, additional method development was necessary to address the analytical needs of the project. When the proposal was submitted, we had developed a method for the extraction and quantification of nonylphenol (NP), octylphenol (OP) and their ethoxylated derivatives with up to 5 ethoxylate units (APnEO, $n = 1 - 5$), which has been published since then (Loyo-Rosales et al 2003). In the last year, we have expanded that method to include NPnEO with $n = 6$ to 16, which are extracted simultaneously to the APnEO with $n = 0$ to 5. The main limitation was the lack of adequate analytical standards for these compounds because they are not available individually, only as technical mixtures. Besides, most of these mixtures are not characterized, and the relative content of each ethoxymer is unknown. We attempted to use Marlophen 810 (Chemische Werke, Hüls, Germany), characterized by Ahel et al (2000), but we discovered that this mixture not only contains the NPnEO, but also the OPnEO, rendering it useless for quantitative purposes. Therefore, we used Surfonic N-95 (Schenectady International, Schenectady, NY), which was characterized by Huntsman Corporation (Austin, TX), and we were able to successfully quantify NPnEO ($n = 6 - 16$). Unfortunately, there are no

characterized mixtures of the OPnEOs available; therefore, we are monitoring these analytes only qualitatively.

As part of the proposed model, it is necessary to quantify the analytes of interest in the particulate matter in the water. We developed an analytical method based on Soxhlet extraction with methanol and LC/MS/MS analysis. In order to obtain the particulate, one liter of water is vacuum-filtered with two pre-weighed glass microfibre filters (GF/A and GF/F, particle retention 1.6 and 0.7 μm respectively, Whatman Inc., Clifton, NJ; previously baked at 400°C for 4 h to eliminate any possible NP contamination) in a glass filter holder (Millipore Corporation, Billerica, MA). The filtrate is used for water analysis of the APnEO and the filters are allowed to dry overnight in a desiccator under vacuum. Once dry, the filters are weighed again to calculate particulate concentration and then spiked with a ^{13}C -labeled internal standard and Soxhlet-extracted with methanol for 8 hrs. The extracts are then evaporated to approximately 5 mL in a rotary evaporator, transferred to 15-mL glass centrifuge tubes and further reduced to 0.5 mL under a gentle nitrogen stream. After adding 0.5 mL of carbon-free deionized water, the extracts are filtered using an Acrodisc LC 13-mm syringe filter with a 0.2- μm PVDF membrane (Pall Gelman Laboratory, Ann Arbor, MI) into a 2-mL LC vial; the syringe and filter are rinsed with 0.5 mL of a 50:50 methanol/water mixture that is added to the extract. Finally, volume is adjusted to 1.5 mL and the extracts analyzed by LC/MS/MS. Recoveries for this extraction method vary for the different compounds and range from 73 to 100%.

Besides the APnEO, we are also interested in modeling other metabolites, such as their carboxylated derivatives. Due to their ionic nature, these cannot be extracted along with the APnEO, and a separate extraction method was developed for them. In this method, water samples are filtered as described above and part of the filtrate is acidified to pH 2 with HCl, and extracted with dichloromethane (DCM) in a separation funnel. DCM is evaporated and exchanged to approximately 5 mL methanol in a rotary evaporator and treated as above. Recovery was calculated for the three carboxylated metabolites (NP0EC, 93%; NP1EC, 93%; and OP0EC, 94%) for which standards are available. Additionally, we have been able to identify

carboxylated derivatives with higher molecular weight, and we plan to monitor them qualitatively.

Theoretical model

For our initial approach, we constructed a model of Back River in a commercial modeling environment (Stella, isee systems, Lebanon, NH). Only NP was considered and the river was divided into four cells (see figure 1). The first and northernmost cell includes the influent from the two major tributaries, Herring Run and North East Creek and ends before Back River WWTP. The second cell includes the effluent from the WWTP and ends at Muddy Gut. The third cell starts at Muddy Gut and ends at Greenhill Cove. The fourth and last cell runs from Greenhill Cove to the mouth of the river into the Chesapeake Bay. The last two cells receive water only from the preceding cell; no other inputs were considered. This division was based on the location of the influents to the river and specific geographic features; i.e. points where the river turns. Each section of the river was modeled as a well-mixed reactor. The following processes were included in each cell: advection, dispersion, volatilization, photolysis, partition into suspended solids and net deposition into sediments. Advection was modeled as a function of flow rate (Q) and concentration (total concentration of the chemical, including both dissolved and bound species). The flow rate was assumed to be constant and values used were ten times smaller than the actual flow rates to account for tidal flow. Dispersion was modeled as a function of concentration gradients between sections, dispersion coefficient – constant for all sections in the river –, cross sectional area and volume of each section. Volatilization was modeled as a flux out of the water, assuming the concentration of these chemicals is equal to zero in the atmosphere. Photolysis of NP and deposition into sediments were modeled as a first order reaction. Flow diagrams of the model are depicted in figure 2.

The preliminary results of our model suggest that, after reaching steady state, NP will be present in the water at a concentration of 0.5, 0.7, 0.4 and 0.08 $\mu\text{g/L}$ for cells 1 to 4 respectively. This

values are very close to actual concentrations measured in the river in January 2001 (0.3, 0.4, 0.2 and 0.05 $\mu\text{g/L}$ respectively). The steady-state amount of NP in the water represents approximately 10 % of the total amount entering the Back River over a period of 10 days. Photodegradation appears to be the most important removal process for NP in the water (49% of the NP entering the Back River), whereas deposition into sediments is the second most relevant process (35%), and volatilization losses are minimal (3%). Even with these losses, 13% of the NP would be transported into the Chesapeake Bay. These results are summarized in figure 3.

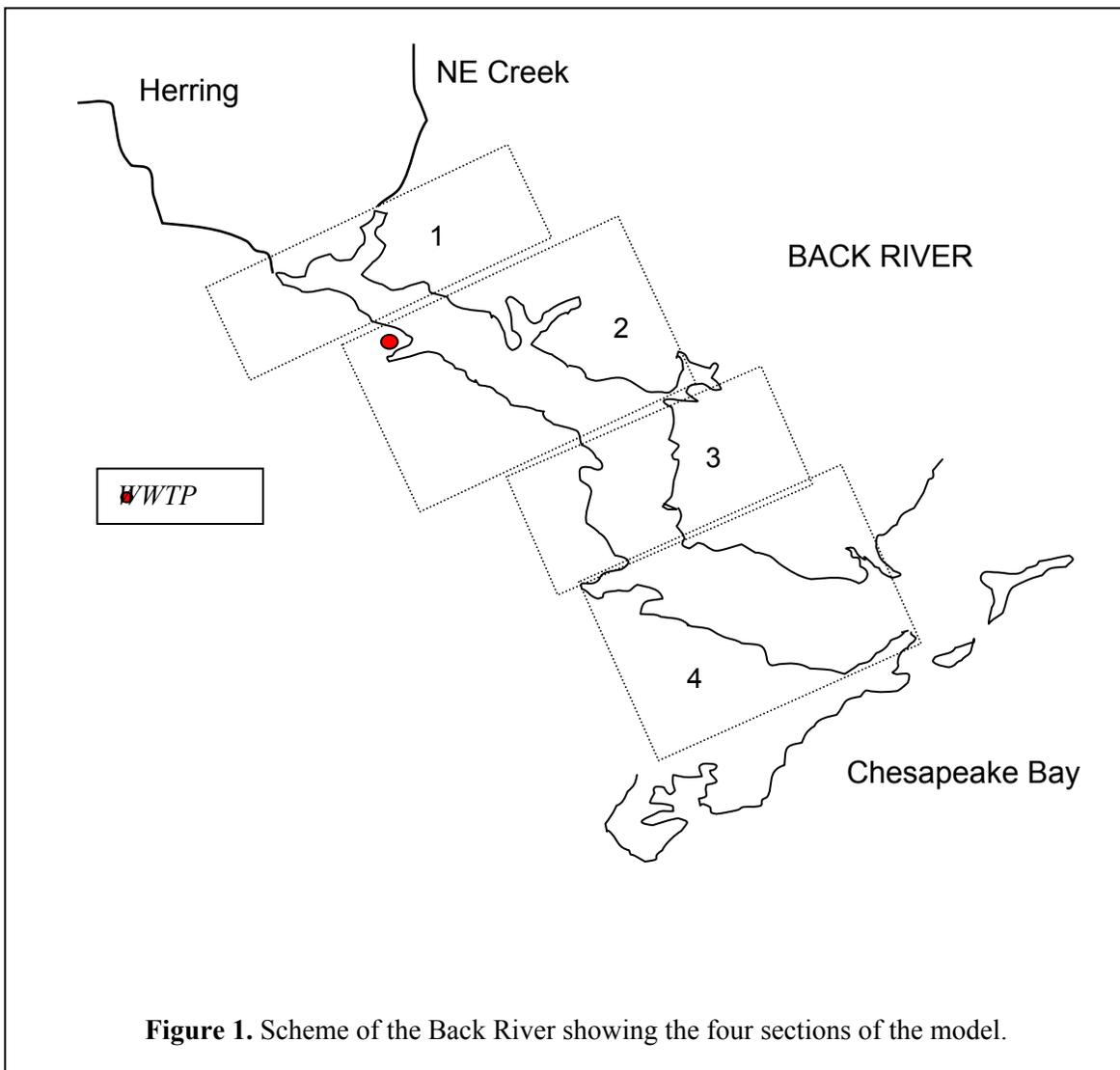


Figure 2. Flow diagram for the Stella model of NP distribution in the Back River.

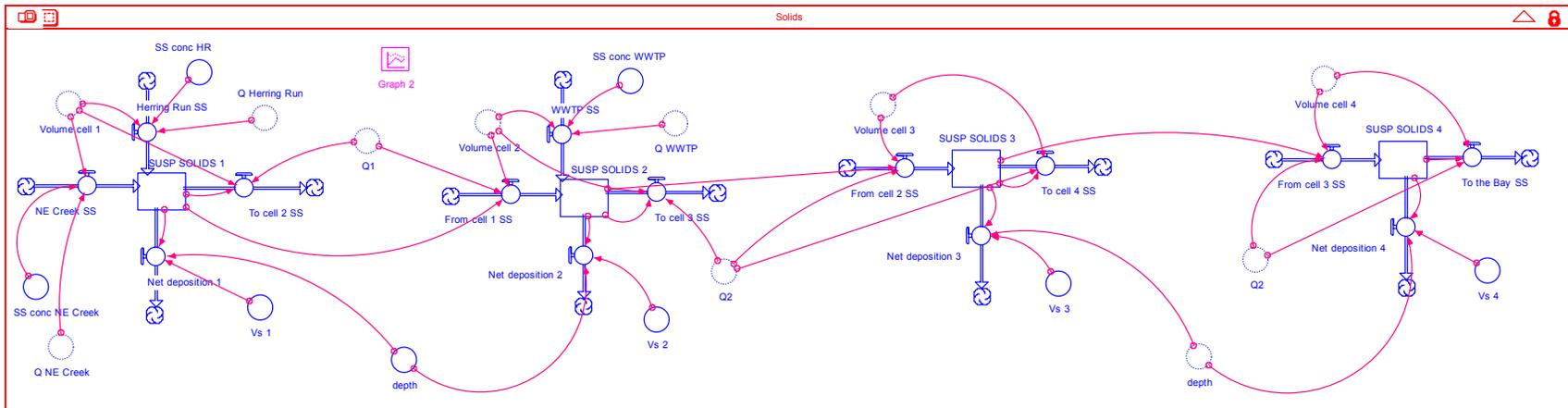
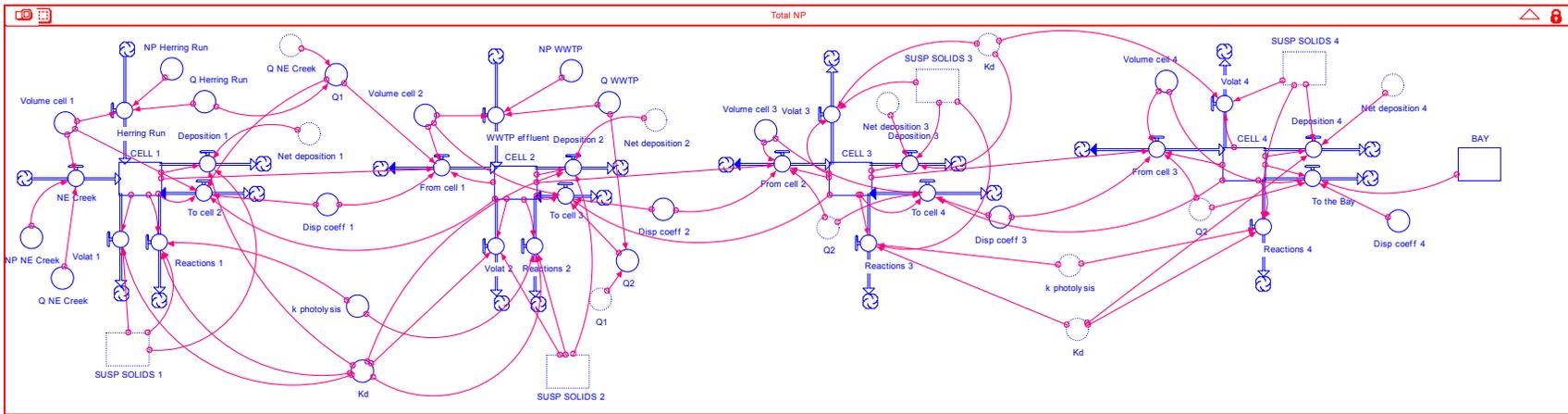
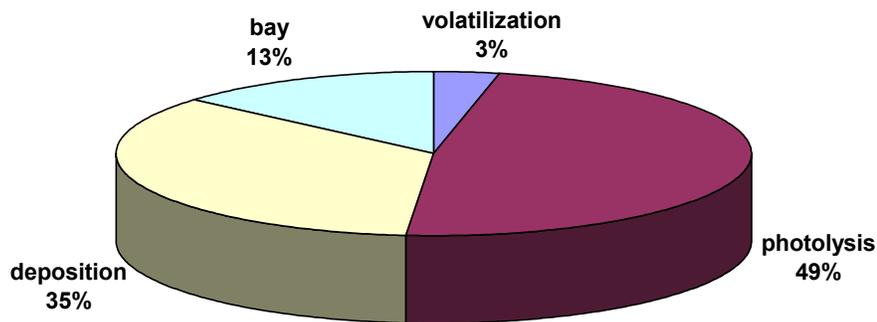


Figure 3. NP distribution in the Back River



Current and future activities

For the second year of the project, we are working on adding more compounds to the model (APnEO) and improving its accuracy by focusing on several items, mainly:

- Adequate quantification of the NP and APnEO inputs into the system. Estimates from previous samplings were used until now; improving the accuracy of these figures will result in better estimates of the equilibrium concentrations in the river. We are currently planning two sampling trips to the Back River that will include collection of both sediment and water along the river. One sampling event will be conducted during the summer and the second one in the winter to account for temperature variations. At the same time, sampling will be conducted at the wastewater treatment plant to better estimate the compounds input to the river.
- A better description of the river's hydrology, including the tidal nature of its flow. We attempt to include variations in the flow and improve our understanding of dispersion in the system.
- The model in its present form does not consider biodegradation. Although it is still debated whether NP is subjected to biodegradation, some studies show evidence that it is. However,

it is widely accepted that APnEO are degraded by microorganisms in the environment and that this is a relevant removal process.

- A better understanding of the suspended solids behavior, including transport along the Back River, deposition and resuspension. These are important parameters, because NP and the lower molecular weight APnEO tend to partition to solids; therefore, the rate at which they are deposited into the sediments has a strong influence on their removal from the water.

Significance

We currently have a sound analytical methodology for the study of NP and degradates. We have also developed a Mass balance and distribution model for Back River. During the second year we will concentrate in obtaining WWTP discharge values and water and sediment values to refine the model and assess the relative importance of all the modeled processes. Once such a model is available, it would be extremely useful for policy makers as they could assess the distribution of NPs in natural systems. Furthermore, the framework of this model could be used to develop models for other emerging organic pollutants.

References

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