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Project Summary

Origin and Chemical Composition of Androscoggin River Foam

Bruce K. Wallin and Brian T. Bisson

A sampling and analysis program on the Androscoggin River and at International Paper Company's Androscoggin Mill in Jay, Maine was undertaken to determine the origin and chemical composition of Androscoggin River foam. The report documents an extremely complex chemical composition of river foam. A mass balance of downstream river foam accounts for approximately 50 percent of both organic and inorganic matter. River samples downstream of both industrial and municipal point sources foamed, but locations upstream of any point sources foamed as well. It could not be determined from the data generated in this study whether any of the industrial or municipal point sources acted alone, or in combination with one another and/or ambient conditions to cause the foaming condition.

The Project Report was submitted in fulfillment of Contract No. 68-03-2605, Work Directives Nos. 2, Part II, and 7 by the E.C. Jordan Co., under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period May 4, 1978 to September 10, 1980, and work was completed as of June 25, 1980.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Background

For some time the rivers of northern New England have been known to be prone to foaming. Foaming on rivers in other areas of the country is less well documented, though there are examples of estuarine foam problems such as Peridido Bay in Florida.

Foam is defined as a dispersion of gas bubbles in a liquid. In order for foam to occur, a critical concentration of a surface active substance must be present. Surface active substances or surfactants are described as molecules having both hydrophilic and hydrophobic groups. The hydrophilic group has a tendency to unite with water, and the hydrophobic group is not capable of uniting with water. This property causes surfactants to concentrate at the gas/liquid interface, thus satisfying both portions of the molecules, and under proper conditions foam is formed.

For many years the State of Maine Department of Environmental Protection (DEP) has received public comments voicing concern about accumulations of foam on the Androscoggin River. Generally, the public has perceived foam as an aesthetic problem introduced to the river by the several pulp, paper, and paperboard mills located on the river. However, sources of surfactants include publicly owned treatment works (POTW) and nonpoint sources, as well as the pulp, paper, and paperboard industry.

Foaming has been an historical problem within pulp, paper, and paperboard mills. Resin and fatty acids were identified years ago in their effluent. Resin and fatty acids are structurally surface active. The concentration it takes to make them surface active (and cause foam) is variable with different compounds and classes of compounds, but the fact remains that resin and fatty acids are surface active.

Publicly owned treatment works (POTW) may also be a source of surfactants. If a POTW treats purely municipal wastes (no industrial contributions), there are two general categories of surfactant contributors - manmade detergents, the sulfonates and neutrals and surfactants that result from biological treatment itself. The metabolic breakdown of the biological treatment process results in the release of fatty acids, and human fecal matter contains fatty acids that are the result of incomplete absorption of the human digestive tract.

Nonpoint sources may also contribute to foaming potential in the river. Agricultural lands may contribute fatty acids from fecal matter on pasture lands. Rural forest lands may also contribute fatty acids from decaying biological materials. Protein, which is a product of any biological process, is somewhat surface active, but it would not be expected to be found naturally in any appreciable quantities in a stream or river.

The Androscoggin River headwaters are in northwest Maine, where it flows eastward from Umbagog Lake through Errol and Berlin, New Hampshire, then back into Maine through the towns of Rumford, Jay, Lewiston, and Brunswick, before discharging to the Atlantic Ocean at Merrymeeting Bay. Three bleached kraft mills and one groundwood mill are located along the Androscoggin's 200-mile length: Brown Company in Berlin, New Hampshire; Boise Cascade Corporation in Rumford, Maine; International Paper Company in Jay, Maine; and Pejepscot Paper Company in Topsham, Maine. Each of the three bleached kraft mills produces pulp at a rate of approximately 1,000 tons per day (tpd), the groundwood mill at a rate of 150 tons per day, and each is served by a secondary wastewater treatment facility.

Study Objectives

Several organizations worked together on the evaluation of Androscoggin River foam. An explanation of how the project unfolded puts the roles of the participants in perspective. First, the public voiced concerns to the State of Maine DEP over foam accumulations on the Androscoggin River. DEP requested assistance from the EPA when the problem was found to be beyond the state's funding and technological capabilities. Since the E.C. Jordan Co. was under contract with EPA, it was retained to study the problem. The DEP was to provide support by performing an ambient sampling and analysis program on the Androscoggin River. Battelle Laboratories was contracted by EPA to assist in the study by elucidation of the Androscoggin River foam. It was felt that the ultimate success of the project depended on a detailed chemical breakdown of the most complex foam, the terminal foam. Daniel W. Armstrong, Ph.D., was subcontracted by E.C. Jordan Co. after some of Battelle's early analyses had begun to uncover the extreme complexity of the foam chemistry. Dr. Amrstrong is a chemist who specializes in surface active material and, therefore, his role in the project was to help with some of the problems of surfactant chemistry.

At the outset of this study, the objectives were defined as follows:

1. Definition of the chemical constituents causing both naturally occurring foams and foams associated with pulp, paper, and paperboard mill discharges;
2. Development, through laboratory and pilot plant studies, of foam removal and treatment technologies capable of yielding non-foam generating mill effluents; and
3. Assessment of the effectiveness of the developed removal and treatment technologies for minimizing and/or eliminating surfactants in mill's final effluent.

Due to the lack of available literature and in-place technology to solve the foam problem, these objectives outlined an ambitious program. During the initial phases of this study, the objectives were redefined as follows:

1. Determine the chemical composition of Androscoggin River foam;
2. Determine the origin of the foam constituents; and
3. Recommend further studies to reduce or eliminate the foaming condition.

A four-phase sampling and analysis program was undertaken to study the river foaming problem.

1. Phase I: The purpose of Phase was to determine if resin and fatt acids were present in a pulp paper, and paperboard mill's ef fluent. The International Pape Company's Androscoggin Mill i Jay, Maine was selected as th pulp and paper mill for sampling Analysis was performed by ga chromatography/mass spectrom etry (GC/MS) utilizing analytica procedures developed by the EPA

   Between Phases I and II a com parison of gas chromatograph (GC) and GC/MS analytical result was made. It was found that G analyses provided accurate, reli able results for a much lower cos than GC/MS analysis could pro vide. This was important to th study because had GC/MS bee required, the higher cost woul have severely limited the numbe of analyses that could be performed This conclusion was borne out by GC versus GC/MS comparison i another EPA study.

2. Phase II: This phase began a proces which was intended to ultimatel lead to meeting study objective by developing "treatment technol ogies capable of yielding non foam mill effluents." Battelle an DEP results had not demonstrate the pulp, paper, and paperboar industry was solely responsible fo the foaming condition on the And roscoggin River. However, it wa known that pulp, paper, and paper board mill effluents foamed, so th first step was to sample in a pulp paper, and paperboard mill to fin the sources of the surfactants This would help by determinin what to treat and where to treat i the rationale being that it would b more economical to treat a singl process stream than to treat all o the process streams together Under Phase II, sampling an analysis was continued at Inter national Paper Company's And roscoggin Mill by analyzing 24 hour composite samples from si locations.

3. Phase III: This phase continued th work of Phase II studying thre sample locations at Internationa Paper Corporation's Androscoggi Mill in more detail. The object wa to observe the day to day variabilit in the mill processes and to chec

the affect of various parameters on foaming tendency of water samples collected in the mill. Parameters were varied that were known to effect foaming tendency, including pH, addition of water softener (hexametaphosphate), addition of sodium, and addition of surfactant (Joy dishwashing detergent). The pH has a dramatic effect on the foaming tendency of surfactants. Water softeners have a higher affinity for metallic ions than surfactants. If left in solution, metallic ions form a complex with certain surfactants rendering them insoluble. Therefore, the addition of water softeners allows any surfactants that are present to more readily create foam. Sodium increases the ionic strength of a solution. Therefore, sodium lowers the critical concentration of a surfactant required to create foam. When surfactants are present in solution below their critical concentration (for creating foam), foam will not form. However, foam may be created by adding more surfactant, such as Joy dishwashing detergent. The foam then concentrates surfactants from both the Joy and the solution's original surfactants.

During Phase II, the bleach plant effluent samples unexpectedly foamed. Two groups of surfactants were found to be responsible: methylene blue active substances (MBAS) and polyaromatic pulping products. Therefore, during Phase III, analyses were performed for these surfactants as well as for resin and fatty acids.

4. Phase IV: It was anticipated that this phase would entail performing a pilot scale foam generation system study. However, the parallel ongoing analysis by Battelle of the terminal river foam had not demonstrated that the pulp, paper, and paperboard industry was solely responsible for the river foam. Therefore, it was inappropriate to do a pilot plant study at International Paper Company's Androscoggin Mill. Instead, the Phase III program was continued on a larger scale by including the sampling and analysis of the major industrial and municipal point sources on the Androscoggin River in Maine.

Foaming is a complex phenomenon. Its composition may include anions, cations, resin acids, fatty acids, and numerous other elements. All of the compounds that form foam on the Androscoggin River have not been identified, nor is there an EPA-approved test to determine the foaming potential of wastewater. However, the redefined objectives of this study have been partially met, and we are much closer to an understanding of foam, and to developing an eventual solution to the problem.

The general accomplishments of this study are as follows. A literature review entitled "Foam and Its Elimination" was completed in April 1979, and is appended. In addition, Battelle Columbus Laboratories of Ohio analyzed collapsed river foam samples in order to chemically characterize the materials present. A large percentage of the materials can be accounted for by summation of individual analyses, as shown in Battelle's report, also appended. However, of these materials that are extractable, only a few percent are accounted for by summation of the individual compounds identified by gas chromatography/mass spectrometry (GC/MS). It is probable that a large portion of the extracted material decomposed in the GC injector even after derivatization.

The State of Maine Department of Environmental Protection (DEP) also performed a study of the sources and causes of foam along the entire length of the Androscoggin River. Generally, organic concentrations were found to be low or undetectable in ambient waters, but the data are insufficient to produce obvious or easily substantiated conclusions. The DEP report is also appended.

Conclusions and Recommendations

The data presented in this report clearly documents the complexity of the foaming problem on the Androscoggin River. An extremely complex chemical composition of riverine as well as upstream pristine foam, ambient factors, and contribution by various point sources all have yet to be fully explored.

At this point in the study of Androscoggin River foam, it has not been determined whether any of the industrial or municipal point sources acting alone, or in combination with one another and/or ambient conditions, is responsible for the foaming condition on the river.

Conclusions

Detailed conclusions may be found in Sections 3 and 4 of the Project Report. The following is a summary of conclusions:

The Chemical Composition of Foam: River foam downstream of Topsham was found to contain a plethora of organic matter, including neutrals, weak acids, polyaromatic pulping products, as well as inorganics. "Pristine" foam (foam upstream of all points sources) lacked certain of the above components, such as resin acids and chloroguaiacols, but was also found to be extremely complex. An attempt to mass balance a downstream sample of foam accounts for approximately 50 percent of both organic and inorganic matter.

Origin of Foam Constituents: The Rumford-Mexico and Lewiston-Auburn municipal treatment plant effluents did not produce collectible quantities of foam when subjected to pneumatic treatment. Most of the pulp, paper, and paperboard mill treatment plant effluent samples produced foam when subjected to pneumatic treatment. The Lisbon municipal treatment plant effluent (which contained paperboard mill treated wastewater) also foamed. Samples foamed for up to one-half hour and then stopped. Collectible foam was found to be enriched in methylene blue active substances (MBAS), while polyaromatic pulping products were not concentrated in the foam.

Factors Affecting Foam Formation: International Paper's Androscoggin Mill was sampled at the brownstock washer effluent (BS) and the bleach plant acid sewer (BP), as well as at the secondary clarifier effluent (FE). The BS effluent contained resin and fatty acids, methylene blue active substances (MBAS), and polyaromatic pulping products, while the BP effluent contained only MBAS and polyaromatic pulping products. Factors known to affect foam formation, including pH, sodium, hexametaphosphate, and addition of surfactants were analyzed for their effect on BS, BP, and FE samples as shown in Table 1.

The table shows that several parameters increase the foaming tendency of the BS and FE effluents. As expected, only the addition of surfactant increased the foaming tendency of BP. The adjustment of pH or the addition of chelating agents should not enhance the BP effluent foaming tendency because strongly acidic or neutral surfactants are not affected by these parameters. The same parameters that enhanced foaming tendency in the BS effluent also increased removals of MBAS, resin and fatty acids by foaming. In the FE the data shows removals of polyaromatic pulping products by addition of a surfactant.

Recommendations

In order to solve the Androscoggin River foaming problem, the sources and chemistry of the foam must be identified. Also, a better method of testing samples for foaming tendency would help in determining the relative contributions.

A better foaming tendency test alone, however, may not solve the problem economically. Mechanical defoaming equipment has been developed that is effective, but economically prohibitive. Therefore, another reason for studying foam chemistry is to determine if there are major foam constituents that could be selectively removed at a reduced cost.

The following seven points suggest further areas of study of the foaming problem on the Androscoggin River:

1. Elucidation of the chemical composition of foam. The Battelle and DEP results indicate that a considerable amount of material in Androscoggin River foam remains to be characterized. Low recoveries of organics, both neutral and acidic, in the extractable fraction suggest that HPLC/MS should be employed. The aqueous phase, with its apparently substantial level of unidentified MBAS should also be studied further using more sophisticated techniques such as HPLC/MS. Additional inquiry into the variability of chemical composition of foam at various points on the river should lead to a clearer understanding of the factors contributing to the foaming condition.
2. The results from chemical analysis of various point sources, ambient foams, and pristine foams should be correlated to determine the origin of contributing surfactants.
3. Determination of the chemical composition of MBAS in various point sources: All samples analyzed contained MBAS which can be strong surfactants. It should also be determined whether the MBAS are of domestic or industrial origin. The action of sulfide ion to accelerate dissolution of wood to release cellulose fibers has been known for many years. The acceleration is chemically described as a reaction between the sulfide ion and lignins. Subsequent to the direct reaction of sulfide in the digester, oxidative reactions can lead to the production of polyaromatic pulping products. The commercial preparation of lignosulfates gave a weak MBAS reaction. It is possible that different forms of organic sulfates and sulfonate surfactants could be produced in the pulping process that would be positive to the MBAS test.
4. Testing of the foamability of pure solutions containing various levels and combinations of the compounds present in river foam should be performed.
5. Development of improved methods for analysis of surfactants: The present methods for the levels of surfactants of the type found in river foam require improvement. In particular, the MBAS, polyaromatic pulping products, and neutral surfactants will require high resolution HPLC coupled with MS for resolution and identification.
6. The effect of ambient conditions, i.e. flows, temperature, humidity, and wind, on the persistence of river foam: DEP has shown a possible correlation to river flow and foaming, but substantiating data has not been collected.
7. Further work should be performed on the following: foam composition as it relates to the possible concentration of toxic substances from the river and its sediments; the resolution, transport and deposition of priority pollutants and other substances by surfactant aggregates; stabilization or destabilization of toxic pollutants and other substances by surfactant aggregates; and the synergistic effect of toxicity of various priority pollutants and other substances when in the presence of surfactants.
8. A method for assessing foaming tendency in ambient conditions should be developed. Two techniques were used in this study: a blender technique as outlined in ASTM D3519-76 and a pneumatic technique developed by B.C. Research. Both techniques are standard techniques that have been used by others. However, both failed to produce foam on some samples which would have been expected to foam because of the observed foaming condition in the river during sampling. Also, both techniques fail to detect trace amounts of surfactants. Therefore, a more sensitive technique should be developed.

Table 1. *Data Summary of Factors Affecting Foam Formation at International Paper Corporation, Jay, Maine*

		Increased Removals by Foaming of		
Sample Location	*Treatment that Enhanced Foaming Tendency*[a]	*MBAS*[b]	*Resin and Fatty Acids*	*Polyaromatic Pulping Products*
BS	*1,2,3,4*	*1,2,3*	*1,2,3,4*	*No*
BP	*4*	*3*	*Limited data*	*No*
FE	*1,2,4*[c]	[d]	[d]	*4*

[a]*Treatment effects of the following four conditions were examined:*
1 = adjusting pH
2 = addition of sodium sulfate
3 = addition of sodium hexometaphosphate
4 = addition of a surfactant (Joy dishwashing detergent)

[b]*Because the surfactant addition, treatment 4, resulted in high levels of MBAS addition, removals of relatively low levels of MBAS in the original solution could not be assessed.*

[c]*The FE did not foam without treatment.*

[d]*Original levels were too low to determine effects of treatment.*

Bruce K. Wallin and Brian T. Bisson are with E. C. Jordan Co., Portland, ME 04112.
***Michael R. Strutz** and **Donald L. Wilson** are the EPA Project Officers (see below).*
The complete report, entitled "Origin and Chemical Composition of Androscoggin River Foam," (Order No. PB 81-208 167; Cost: $18.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officers can be contacted at:

Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
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Information
Cincinnati OH 45268

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230 S DEARBORN ST
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