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Project Summary

Fate of Toxic and Nonconventional Pollutants in Wastewater Treatment Systems Within the Pulp, Paper, and Paperboard Industry

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Field studies were undertaken to determine the fate of toxic and nonconventional pollutants present in the wastewaters discharged from the pulp, paper, and paperboard industry. A sampling and analysis program was conducted at two deink mills and a groundwood fine papers mill. Each mill employed a wastewater treatment system which included primary clarification, high rate biological treatment, secondary clarification, and combined primary/secondary sludge dewatering.

Through a sampling program of primary clarifier influent, biological treatment effluent, air emissions above the aeration tanks, and dewatered sludge solids it was the objective of the study to complete a mass balance of the pollutants under study.

Analysis of primary clarifier influent samples was by both GC and GC/MS techniques; analysis of the remaining samples was GC method alone.

In general, 50 percent of the mass of each pollutant found in the mill's raw wastewaters were accounted for in the program. The accountability of the volatile organic pollutants ranged from 27 to 55 percent. The accountability of semi-volatile pollutants ranged from 6 to 933 percent with three pollutants accounted for in excess of 100 percent.

This report was submitted in fulfillment of Contract No. 68-03-2605, Work Directive No. 3, by the E.C. Jordan Co. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1978 to June 1980, and work was completed as of June 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

Program Objectives

Under Work Directive No. 3 the fate of the toxic and nonconventional pollutants present in the wastewaters discharged by the pulp, paper, and paperboard industry was to be determined. As specified by the Agency, the E.C. Jordan Co. was to sample "bottom sediments,

air emissions and wastewater input and output for biological treatment systems treating unbleached kraft - hardwood and softwood, bleached groundwood integrated pulp mills and for NSSC only pulp mills." These biological or physical-biological treatment systems were to be sampled for toxic pollutants and other chemicals directed by the Agency but including those toxic pollutants detected during the EPA Effluent Guidelines Divisions' Best Available Technology Economically Achievable (BATEA) Review Program.

Due to the budgetary limitations the E.C. Jordan Co. initially recommended that only semivolatile acid-neutral compounds (SV-AN) be studied in Work Directive No. 3. This recommendation was made since available data indicated that the volatile organics were removed by aeration, and benzidine was the only basic semivolatile organic detected previously in pulp, paper, and paperboard mill wastewaters. In the final formulation of the work program it was recommended that the raw wastewater samples be screened by gas chromatograph/mass spectrometry for all volatile and acid-neutral semivolatile organic pollutants previously under study in the Agency's BATEA Review Program. The compounds under investigation are presented in Table 1.

Based on information gathered during the Effluent Guideline Division's study, the Jordan Company recommended that the subcategory selection be modified to include the following:

1. Bleached kraft,
2. Unbleached kraft (softwood),
3. Bleached groundwood, and
4. Deink.

The above recommendations were made because the wastewaters from these subcategories were known to normally contain, among others, measurable quantities of the toxic and nonconventional organic pollutants of concern.

The E.C. Jordan Co. also recommended that only mills employing the conventional activated sludge process for wastewater treatment be considered in the response to the work directive. Aerated stabilization basin systems were deemed unacceptable, because mass balances associated with suspended solids in the treatment system could not readily be addressed as a result of the material partially settling out in the system's aeration basins. Pure oxygen activated sludge systems were also deemed inappropriate for investigation because of the enhanced probability of molecular oxidation of the subject pollutants by contact with high concentrations of pure oxygen.

Table 1. *Toxic and Nonconventional Pollutants in the Pulp, Paper, and Paperboard Industry*

Toxic Pollutants

Volatile Organics
- *benzene*
- *bromoform*
- *carbon tetrachloride*
- *chlorobenzene*
- *chloroform*
- *dibromochloromethane*
- *dichlorobromomethane*
- *1, 1-dichloroethane*
- *1, 2-dichloroethane*
- *ethylbenzene*
- *methylene chloride*
- *1, 1, 2, 2-tetrachloroethane*
- *tetrachloroethylene*
- *toluene*
- *1, 1, 1-trichloroethane*
- *trichloroethylene*
- *trichlorofluoromethane*
- *xylene*

Semivolatile Organics
- *acenaphthene*
- *acenaphthylene*
- *anthracene*
- *bis(2-ethylhexyl)phthalate*
- *butyl benzyl phthalate*
- *2-chlorophenol*
- *chrysene*
- *2, 4-dichlorophenol*
- *diethyl phthalate*
- *di-n-butyl phthalate*
- *2, 4-dinitrophenol*
- *di-n-octyl-phthalate*
- *fluoranthene*
- *isophorone*
- *naphthalene*
- *p-chloro-m-cresol*
- *pentachlorophenol*
- *phenol*
- *pyrene*
- *2, 4, 6-trichlorophenol*

Nonconventional Pollutants

Resin acids
- *abietic acid*
- *dehydroabietic acid*
- *isopimaric acid*
- *pimaric acid*

Fatty acids
- *oleic acid*

Bleach plant derivatives
- *dichlorodehydroabietic acid*
- *monochlorodehydroabietic acid*
- *3, 4, 5-trichloroguaiacol*
- *tetrachloroguaiacol*

Eight mills in the aforementioned four recommended subcategories were contacted by the E.C. Jordan Co. and asked to participate in the program. Of the eight mills contacted, favorable replies were received from three deink fine paper mills and three groundwood fine paper mills. The remaining two mills did not desire to participate in the program. Of the six favorable responses three mills were selected to participate in the program. Several of the responding mill personnel, in responding to the E.C. Jordan Co.'s request to participate, noted that, due to the level of pollutants present and process variations, a complete "pollutant closure" would be difficult. However, personnel felt that useful data would be gathered relative to the toxic and non-conventional pollutants. The mills participating in the program are indicated below:

Subcategory	Mill Name and and Location
Deink	Bergstrom Paper Company Neenah, WI
Deink	Wisconsin Tissue Mills, Inc. Menasha, WI
Groundwood-bleached	St. Regis Paper Company Sartell, MN

To accomplish the goal of the work directive, a sampling and analysis program was developed which would allow for the calculation of pollutant mass balances across the three wastewater treatment systems investigated. Each system included primary clarification, high rate biological treatment,

secondary clarification, and combined primary/secondary sludge dewatering.

Prior to finalizing the sampling and analysis program, the E.C. Jordan Co. reviewed with Agency representatives the pollutants of potential concern in the pulp, paper, and paperboard industry. It was decided that raw wastewaters would be screened by GC/MS for all of the pollutants (see Table 1). The air, sludge, and final effluent samples would be analyzed by GC for those pollutants detected in the raw wastewater by GC/MS procedures.

The program utilized in this study involved the collection of samples from the following locations at each of the three facilities investigated:

1. primary clarifier influent;
2. secondary clarifier effluent;
3. air emissions above the aeration tanks; and
4. dewatered sludge solids.

Analysis of primary clarifier influent samples was by both GC and GC/MS techniques; analysis of the remaining samples was by the GC method alone.

Origin of Specific Toxic Compounds

Specific toxic compounds in the raw materials and the wastewaters from various mills in the pulp, paper, and paperboard industry, and from the wood products have been reported in the literature. Most of the literature, however, has dealt with the toxicity of various resinous and fatty acids (see Table 1).

One study found that resin acids contribute substantially to the toxicity of wastewaters from all pulping processes. A similar study summarized the resin and fatty acid contents of major wood species used in the industry. The results, summarized in Table 2, show that pines have by far the highest acid content of species studies.

The content of total resin acids was also observed to vary within the major species groups. One study showed a substantial variation in resin acid content for trees of different ages. It was shown also that resin acid content was a function of tree diameter, i.e., the larger the diameter, the higher the resin acid content.

Also of concern are heavy metals. These primarily originate from pigments added in paper coating and glazing operations. There is a lack of literature on specific toxicity of additives used in various papermaking operations.

Table 2. Typical Resin and Fatty Acid Contents of Raw Wood Types

Species	*Total resin acids (Percent by weight oven dried wood)*	*Total fatty acids (Percent by weight oven dried wood)*
Pines	1.5%	1.0%
Other softwoods	0.1%	0.1%
Hardwoods	negligible	0.5%

Detergents used for deinking of wastepaper also contribute to toxicity. It was determined that several such detergents were lethal to fish at a concentration of 4.0 mg/l. Polychlorinated biphenyls (PCB), formerly used in the manufacture of carbonless copy paper and printing inks, remain in some wastepaper mill effluents because of wastepaper recycling. The New York State Department of Conservation conducted a study concerning PCB in wastepaper mill effluents. Of the 40 New York mills using wastepaper, 18 were determined to be potential direct dischargers of PCB. Final effluent samples from these mills were analyzed monthly from October 1976 to September 1978. The results of this study indicated that final effluent PCB concentrations were generally below one microgram/liter (μg/l) and that the concentration was reduced by biological treatment.

Conclusions and Recommendations

The objective of the program was to determine the fate of a number of toxic and nonconventional pollutants normally present in pulp, paper and paperboard wastewaters. Through a detailed sampling program of influent and effluent wastewaters, air emissions, and solid wastes, it was the objective to complete a mass balance of the pollutants.

In general, 50 percent of the mass of each pollutant found in the mill's raw wastewaters were accounted for in the program. The accountability of the volatile organic pollutants ranged from 27 to 55 percent. The accountability of semivolatile pollutants ranged from 6 to 933 percent with three pollutants accounted for in excess of 100 percent.

Based on the accountability of pollutants experienced in the program, it is apparent that the objective was not achieved due to several factors. These factors include:

1. biochemical transformation;
2. laboratory analysis;
   a. quantity of pollutants,
   b. detection limits,
   c. sample matrix, and
   d. analytical procedures;
3. sampling procedures; and
4. capability to accurately estimate air and sludge emissions.

The impact of several of the factors encountered in this program may be minimized with continued research and controlled conditions.

Future studies of the fate of toxic and nonconventional pollutants in industrial wastewaters should strive for improved accountability of pollutants under study. It is unrealistic to anticipate 100 percent accountability; however, through more controlled conditions, more advanced sampling techniques, and higher resolution analytical techniques, improved accountability should be a realistic goal.

Sampling procedures in future programs should consider flow proportional aliquots (wastewater), composite or individual samples of sludge (solids), and a more efficient air emissions sampler (air).

A statistical design of the sampling program should be considered for future programs. Through consideration of known variables, the sample sites, frequency and number of samples could be considered so that the results will have a known reliability.

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***Michael D. Strutz** and **Donald L. Wilson** are the EPA Project Officers (see below).*
The complete report, entitled "Fate of Toxic and Nonconventional Pollutants in Wastewater Treatment Systems Within the Pulp, Paper, and Paperboard Industry," (Order No. PB 81-247 405; Cost: $11.00, subject to change) will be available only from:

National Technical Information Service
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