Pulp and paper industrial effluents: Toxicity abatement for aquatic life protection

Rosalina P. A. Araujo, Eduardo Bertoletti, Maria de Lourdes L. C. Ramos, Elenita Gherardi-Goldstein, Maria Helena R. B. Martins

Cetesb (Companhia de Tecnologia de Saneamento Ambiental), São Paulo, SP 05459, Brasil

The acute toxicity of the final effluents from the six largest pulp and paper industries located in the State of São Paulo was evaluated with a microcrustacean, *Daphnia similis*, a fish, *Cheirodon notomelas* and an alga, *Chlorella vulgaris*. Most samples showed a relatively low acute toxicity and varied according to the studied species. Results of the study served as the basis for a biological guideline for aquatic life protection.

Foi avaliada a toxicidade de seis efluentes finais de indústrias de papel e celulose do Estado de São Paulo com uma espécie de microcrustáceo, ***Daphnia similis****, uma de peixe,* ***Cheirodon notomelas****, e uma de alga,* ***Chlorella vulgaris****. Foi observada baixa toxicidade na maioria das amostras, variando desse acordo com a espécie estudada. Os resultados do estudo serviram de base para o estabelecimento de critérios biológicos para a proteção da vida aquática.*

The extraction of cellulose from wood requires a large volume of water which, when discharged into the environment, can cause an adverse ecological impact.

In Brazil, trees of the genus *Eucalyptus* are used for pulp production, and about 500 varieties and subspecies grow in different environmental conditions. Because they have fast growth rates (1), this genus has been widely planted in Brazil to guarantee a continuous wood supply for the pulp and paper industry (2). Pulp mills use mainly the Kraft (sulphate) process producing final effluents which have high BOD, turbidity, color, suspended solids and low dissolved oxygen concentrations.

The complex chemical composition of these effluents includes dissolved organic and inorganic substances, sulfurous organic compounds and chlorinated compounds when the pulp is bleached. Many of these compounds have not been identified chemically but may potentially be hazardous to aquatic organisms and impair other uses of receiving water bodies (3).

The interactive effect of all the substances present in pulp mill final effluents can be evaluated using toxicity tests with representative aquatic species. Results of aquatic tests have been used in some countries as one of the criteria to evaluate the pollution potential of industrial effluents (4-8).

The present study was initiated to evaluate the toxicity of the final effluents from the main Kraft pulp and paper mills in the State of São Paulo and to develop toxicity-based criteria for the discharge of these effluents in the environment. Thus the acute toxicities of final effluents from the selected industries were assessed with three test species representing different trophic levels: a fish, a microcrustacean and an alga.

Six pulp and paper mills were categorized according to three general types of process (Table 1).

Samples of final effluents were collected hourly over a six to twelve hour period. Polyethylene flasks were completely filled with effluent, stoppered and kept on ice until arrival at the laboratory, where they were transferred to a refrigerator and held at 4°C. The samples to be tested were prepared proportionally according to effluent flows measured during sampling. They were then split for physico-chemical analyses and for toxicity testing. Tests were started within 24 h after sampling.

Effluent flows were measured through the limnimetric method or radioactive tracer ^{82}Br (9) and the physico-chemical analyses were conducted according to Standard Methods (10). Toxicity tests were conducted using three organisms: an indigenous species of fish, *Cheirodon notomelas*, Eigmann, 1915, according to the ISO static method (11), slightly modified (12); a microcrustacean, *Daphnia similis*, Claus, 1876, tested through the ISO (13) method, modified (12); and an alga, *Chlorella vulgaris* following the method described by Brusick and Young (14), modified (12). Due to the presence of algae, effluents were filtered through a 0.45 μm membrane (15).

Correspondence to: Rosalina Pereira de Almeida Araújo, Cetesb (Companhia de Tecnologia de Saneamento Ambiental), Av. Prof. Frederico Hermann Jr. 345, São Paulo, SP 05459, Brasil

Table 1 — Summary of data for Kraft mills.

Processes in mill	*Production, tons of pulp /day*	*Industry*	*Wood*	*Effluent flow (m^3/s)*	*Receiving body of water(Class)*	*7Q10[a] (m^3/s)*	*Treatment*
Bleached Kraft	630	A	Eucalyptus	1.162	Moji-Guaçu(class 2)[b]	15.20	Settling/Aeration pond
Bleached and unbleached Kraft	116	B	Eucalyptus	0.288	Paraíba (class 2)	25.8	Settling/Stabilization pond
	450	C	Eucalyptus	0.421	Paraíba (class 2)[b]	62.4	Neutralization/Primary settling pond/Aeration pond/Secondary settling
	900	D	Eucalyptus	1.128	Taiaçupeba (class 3)[b]	1.13	Settling pond/Aeration pond/ Bleachment pond
	600	E	Eucalyptus	0.516	Piracicaba (class 2)	21.6	Settling/Stabilization pond/ Aeration pond
Bleached and unbleached Kraft	30	F	Pine Eucalyptus	0.158	Paraíba (class 2)	61.4	Stabilization pond

[a] 7Q10 = mean daily flow of the receiving body of water during the 7-d, 10 y low flow
[b] class 2 and 3 = designated uses for water include the preservation of fauna and flora

Reconstituted water with a total hardness of 40-48 mg/L as $CaCO_3$ was used as dilution water in the tests with fish and microcrustaceans (10).

The fish and *D. similis* tests were performed with at least two samples from the final effluents from each of the six selected industries, sampled at different dates. Algal tests were conducted on effluent samples from only two industries.

Toxicity results for fish are reported as 24-h or 48-h LC50, the concentrations causing 50% lethality of the test organisms after the specified period and expressed as percentages of effluent volume in the test solution. For *D. similis* the 24-h EC50, the concentration which immobilizes 50% of the test organisms, was used.

Some of the fish and *D. similis* tests gave responses of only 10% to 30% immobilization or lethality in high effluent concentrations. Such responses were described as showing "signs of toxicity".

Test results for algae were expressed as 120-h EC50, that is, the concentration that would inhibit growth by 50%, relative to control.

Effluents from industries A, C, D and E presented signs of toxicity or were not acutely toxic to *D. similis*, but samples from industry B were highly toxic to this organism (Table 2). Effluents from industries A, B, C and F were not acutely toxic or presented signs of toxicity to the fish *C. notomelas*. The most toxic samples for fish were from industries E and D, although on some occasions no signs of toxicity to fish were detected in these industries.

Dissolved oxygen levels (Table 2) were in agreement with the minimum levels established by the methods, above 5.0 mg/L for fishes (11) and 2.0 mg/L for *D. similis* (13). Exceptions were *D. similis* tests with effluents from industry D and with the sample collected on 08.30.84 in industry E.

The algal tests showed that the effluent from industry A was inhibitory to *C. vulgaris* growth (Table 3), but there was not a clear response to the effluent from industry B. Methodological difficulties, not only with sample preparation but also during the test (12) limited the number of algal tests that could be performed with the pulp and paper mill effluents.

The tested effluents were usually lightly colored (70 to 1,560 mg Pt/L), with exception of the one from plant C which had a stronger color (3,000 and 2,000 mg Pt/L), characteristic of this type of waste. The effluent of plant C also had the highest BOD and COD levels (178 mg/L BOD and 903 mg/L COD), which were lower in other effluents (36 to 102 mg/L BOD and 169 to 443 mg/L COD). The concentrations of phenol, ammonia, mercury, nitrate, nitrite and pH were low

Table 2 — Results of toxicity tests with fish and microcrustacean

Industry	*Sampling dates*	***Daphnia similis*** *24 h EC50 (%)*	***Cheirodon notomelas*** *48-h LC50 (%)*	*D.O. (mg/L)[a]* ***Daphnia***	***Fish***
A	07.16.84	N.T.[b]	S.T.[c]	3.3	7.8
	10.15.84	N.T.	N.T.	-[d]	-
	01.15.84	N.T.	N.T.	4.2	-
B	08.22.84	17.5 (12.5-24.6)[e]	N.T.	4.0	-
	11.28.84	10.0-37.0	S.T.	4.2	-
	01.09.85	17.0 (13.5-21.4)	N.T.	6.1	7.2
C	09.26.84	N.T.	N.T.	-	-
	12.05.84	N.T.	N.T.	-	
D	04.11.84	S.T.	83.2[f]	1.0	
	11.26.84	S.T.	Unsatisfactory result	0.0	-
	12.04.84	S.T.	N.T.	0.0	-
E	08.30.84	S.T.	58.9	1.4	5.5
	10.25.84	N.T.	69.2	3.0	7.1
	01.22.85	S.T.	90.0 (83.3-97.2)	2.5	7.2
	04.01.85	N.T.	S.T.	-	-
F	08.29.84	N.T.	N.T.	-	-
	11.21.84	Unsatisfactory result	S.T.	-	-

[a] Value at the end of the test in the concentration closest to the LC50 or EC50
[b] N.T. = Not acutely toxic
[c] S.T. = Signs of toxicity
[d] dash - indicates no analyzed samples
[e] parentheses : confidence limits (95%)
[f] 24-h LC50

Table 3 — Test-results for growth of *Chlorella vulgaris*

Effluent concentrations, v/v (%)	Industry A: *No. of cells/mL x 10⁶*	Industry A: *Growth inhibition relative to control (%)*	Industry B: *No. of cells/mL x 10⁶*	Industry B: *Growth inhibition relative to control (%)*
100	7.96	24.6	8.06	14.2
75	5.82	44.9	8.80	6.3
56	6.27	40.6	8.19	12.8
32	8.44	20.1	8.64	8.0
10	7.48	29.2	14.90	(58.6)[b]
5.6	4.72	55.3	8.45	10.0
3.2	6.47	38.7	9.56	(1.8)[b]
1.0	-[a]	-[a]	8.49	9.6
Control (culture medium)	10.56	0	9.39	0

[a] not analyzed
[b] percent growth stimulation

for all samples (Table 4).

Toxicity tests showed that the effluents from the selected pulp and paper mill industry had, in general, low acute toxicity to *D. similis* and *C. notomelas*. Only the effluents from industry B were highly toxic to *D. similis*. These two species responded differently to the effluent samples (Table 2). A difference in species sensitivity has also been observed by other authors (16,17).

The physico-chemical analyses performed during this project were restricted to the regular parameters used by Cetesb for pollution control purposes. Chemicals of a toxic nature such as acid resins, chlorinated compounds and fatty acid agents were not investigated.

The BOD and COD data of the effluents were two to five times lower than those reported in similar studies (18,19). The same was observed regarding their color. Soniassy et al (20) observed that bleached Kraft effluents had color levels ranging from 2,000 to 3,700 mg Pt/L. The only sample that showed such values in the present study was that of industry C. These data and the low values of other analyzed physico-chemical parameters (Table 4) could not explain, by themselves, the toxic effects observed for *C. notomelas* and *D. similis*.

The growth of *C. vulgaris* was slightly affected in several dilutions of effluent from industry B (Table 3), characterized by inhibitions of 6 to 14% when compared to the control. Industry A effluent caused an inhibition of 20 to 55% at all the tested concentrations. The absence of correlation between concentration and response made it impossible to calculate the 120-h EC50. The results of analysis of the physico-chemical parameters (Table 4) from these two effluent samples do not explain the difference of the observed response on both algal tests since the nutrient levels and the values for color, pH and BOD were similar in the two samples.

Despite the relatively high concentrations of ammonia and orthophosphate in both effluent samples, no significant growth stimulation occurred except for the concentration 10% of effluent B. Similarly, Walsh et al (21) did not find correlation between high nutrient concentrations in complex industrial effluents and stimulation of algal growth.

Effluents from industries A and B affected the three test species differently. The effluent from industry A

Table 4 — Physical and chemical data on pulp and paper effluent samples

Parameter	A			B			C		D		E			F	
	1984		*1985*	*1984*		*1985*	*1984*		*1984*		*1984*		*1985*	*1984*	
	07/16	*10/15*	*01/16*	*08/23*	*11/28*	*01/09*	*11/26*	*12/04*	*09/27*	*12/05*	*08/30*	*10/25*	*04/01*	*08/29*	*11/21*
Color (mg Pt/L)	850	900	100	70	800	700	3,000	2,000	1,650	750	600	1,000	675	400	900
BOD (mg/L)	36	41	43	51	48	40	179	98	38	99	84	37	48	93	102
COD (mg/L)	276	263	281	169	198	225	903	757	443	305	337	344	286	320	324
Phenols (mg/L)	[a]	-	0.033	-	-	0.006	-	-	-	-	-	-	0.011	-	-
Total Phosphate as P (mg/L)	1.10	1.70	1.52	0.09	0.65	0.23	1.05	0.80	0.80	0.55	4.25	3.40	4.40	0.46	4.50
Orthophosphate as P (mg/L)	0.60	0.15	0.48	0.04	0.12	0.20	0.58	-	0.30	0.35	0.18	1.95	2.80	0.13	0.37
Mercury (µg/L)	0.4	0.3	0.2	ND[b]	ND	ND	ND	ND	1.4	ND	-	ND	ND	-	ND
Ammonia as N (mg/L)	9.0	1.5	1.3	0.8	1.0	0.4	-	1.7	8.2	1.5	4.4	0.2	19.0	2.1	1.4
Nitrate as N (mg/L)	0.05	0.01	0.17	0.01	0.04	19.30	0.03	0.03	0.01	15.28	0.02	0.04	0.02	1.03	0.01
Non filterable residue (mg/L)	-	-	0.76	-	-	ND	-	-	-	-	-	-	-	0.12	-
Nitrite as N (mg/L)	-	0.01	-	-	ND	0.01	-	0.01	-	0.01	-	ND	0.02	-	-
Conductivity (mS/cm)	2.1	1.8	1.2	0.8	7.3	0.6	1.9	1.6	2.0	1.7	2.4	2.1	1.5	0.4	0.5
pH	7.4	7.5	7.2	7.5	7.5	7.5	8.0	7.9	7.3	7.6	8.0	7.7	7.5	7.4	7.6

[a] Dash = No samples analyzed
[b] ND = Not detected

Table 5 — Impact assessment caused by effluents on receiving water

Industry	A	B	C	D	E	F
LC50 or EC50 (%)	100.00	17.0	100.0	83.2	58.9	100.0
Instream waste concentration (IWC)[a] (%)	7.1	1.1	0.7	49.9	2.3	0.2
No acute effect concentration (%)	33.3	5.67	33.33	27.27	19.63	33.33
Potential for instream acute toxicity	None	None	None	Yes	None	None
No chronic effect concentration (%)	10.0	1.7	10.0	8.32	5.89	10.0
Potential for instream chronic toxicity	None	None	None	Yes	None	None

$$^{a}\mathrm{IWC} = \frac{\text{Effluent flow } (m^3/s)}{\text{Effluent flow } (m^3/s) + 7Q10\ (m^3/s)} \times 100$$

was not acutely toxic to fish and *D. similis* but inhibited algal growth while the effluent from industry B, which was toxic to fish and *D. similis*, did not have an effect on algae.

Freshwater bodies in the State of São Paulo are divided, according to their uses, into four classes, and although water quality standards have been designated for each class since November 22, 1977 (Act n. 10755) (22), our results show a need for toxicity standards for water quality and discharge of effluents.

These Kraft mills discharge their effluents into rivers of classes 2 and 3 (Table 1), the designated uses of which include the preservation of fauna and flora. Most physico-chemical characteristics are compatible with the discharge standards (Table 4) but still the effluents from industries B, D and E were toxic to at least one of the test species used (Table 2). Accordingly, there is a need for regulations concerning toxicity of effluents, besides the existing physico-chemical emission standards for safe discharge of effluents to bodies of water of classes 2 and 3.

Other countries have successfully characterized effluents by analytical methods plus toxicity tests. In France, effluent toxicity is evaluated through *Daphnia magna* toxicity tests and the result, expressed as 24-h EC50, is referred to as "inhibitory materials" which, together with other data such as nutrients, oxidizable materials and suspended solids, are used to tax the effluents discharged into bodies of water(5). In Germany, the toxicity of industrial effluents to fish and *Daphnia* in also evaluated and used as a tool for control of toxicants (8). In Canada the control of industrial effluents is conducted under a federal law which prohibits the discharge of substances deleterious to fish or to human use of fish. In Canada guidelines and regulations were developed for some industrial categories, among which the pulp and paper industry (4). Effluent limitations are expressed in terms of the allowable discharge of given weight of contaminant per unit of production for two or six chemical parameters along with a toxicity limit requirement. These limits were established based on the best available technology for effluent treatment (23).

Some of the Kraft mills in São Paulo treat their effluents to such a level that no acute toxicity is observed in two species belonging to different trophic levels of the aquatic ecosystem (Tables 2 and 3). So, by following the Canadian approach, it could be established that "in the State of São Paulo, effluents from pulp and paper industry should not cause acute toxic effects on aquatic organisms". According to such a guideline, only the effluent from industry C would be considered satisfactory for discharge into aquatic environments. The effluents from industries A, D, E and F would need further treatment to comply with this guideline.

In the United States, industrial effluent control is directly related to the preservation or recovery of natural water quality (6,7). Control of toxicants in industrial effluents is achieved by estimating the concentration of effluents in the environment and comparing it to the measured concentration that caused deleterious effects on representative aquatic organisms. Thus it is possible to estimate the hazard or impact on the environment and take the necessary measures to prevent it.

Following the American approach, the concentration of each effluent in the receiving body of water was estimated, taking into account minimum flow conditions (7Q10) and assuming complete mixture of the effluent (7).

The estimated environmental concentration was then compared to 1/3 and 1/10 of the acutely lethal effluent concentrations. Those fractions of the LC50/EC50 are estimated to be the highest allowable effluent concentrations to prevent, respectively, acute and chronic effects on aquatic biota. The most toxic sample from each effluent was used in this comparison which is presented in Table 5. For effluents that showed only signs of toxicity or no acute toxicity, the most critical situation was considered, that is, a situation in which 100% effluent causes a deleterious effect on 50% of the test organisms. It can be seen from Table 5 that only the effluent from industry D can cause acute and chronic effects on the aquatic biota in the receiving body of water. Although it is not expected that the other effluents could cause a serious impact on the aquatic environment, it is recommended that effluents that are toxic or highly toxic to at least one test species such as effluents B and E be more thoroughly studied, specially with regard to the presence of persistent and/or mutagenic substances.

Some final considerations are needed to select the best approach for the State of São Paulo for the protection of aquatic life. This can be illustrated by the sample of industry D. This effluent presented a very low level of acute toxicity in most samples and, probably, a small change in or a minor upgrading of the treatment process would make it possible for the industry to comply with a possible guideline, following the Canadian approach: "no acute lethality should be detected in pulp and paper effluent". Even then, the lack of acute toxicity does not necessarily imply the absence of chronic toxicity, since the flow of this effluent in relation to the river flow is very high.

The possibility of chronic deleterious effects is not eliminated if the American approach is used. Thus, the

American model, seems the most promising at the present moment, as it considers available dilution in a particular body of receiving water.

The toxicity of pulp and paper effluents should be evaluated with two or more species of aquatic organisms, such as one species of microcrustacean and one species of fish. This is needed because aquatic organisms vary in sensitivity to toxicants.

Although most of effluent samples showed a relatively low toxicity, in one case the flow was high enough to cause acute and chronic effects for aquatic organisms in the receiving body of water. Considering this information, it is suggested that the State of São Paulo should begin to adopt a control procedure that takes into account characteristics such as available dilution in the environment where the effluent is discharged. ■

References and notes

1. Hills WE 1972 Review article: formation and properties of some wood extratives. *Phytochemistry* 11: 1207-1218
2. Bugajer S 1979 Pastas celulósicas sulfato branqueadas de folhosas -- ênfase especial ao eucalipto brasileiro. *O Papel*, Agosto: 47-48
3. McLeay DJ, AB McKague and CC Walden 1986 *Aquatic toxicity of pulp and paper mill effluent. A review*. DL MacLeay & Associates Ltd., West Vancouver BC
4. Environment Canada 1972 *Guidelines for the pulp and paper effluent regulations*. Environmental Protection Service Report Series. Ottawa, Ontario. Environment Canada. (Regulations, Codes and Protocols Report EPS 1-WP-72-2).
5. France 1983 *Pollution des eaux: redevances*. Journal Officiel de la Republique Française. Paris. 5th ed 112 pp.
6. United States Environmental Protection Agency 1984 *Technical support document for water quality-based toxics control (Draft)* US Environmental Protection Agency, Washington, DC
7. United States Environmental Protection Agency 1985 *Methods for measuring the acute toxicity of effluents to freshwater and marine organisms*. US Environmental Protection Agency, Cincinnati, Ohio. (EPA/600/4-85/013)
8. Karbe L 1984 Biological monitoring of water in the Federal Republic of Germany. Regulatory approaches and methods for effluent testing and assessment of receiving waters. *In Proceedings of International Workshop on Biological Testing of Effluents*, p 123-132, Duluth, Minnesota
9. Agudo EG, W Sanchez, JL Santos, S Nakahira, RP Gonzalez 1979 *Calibração e aferição de calhas Parshall por meio de traçadores radioativos*. Cetesb, São Paulo; Congresso Brasileiro de Engenharia Sanitária e Ambiental, Manaus, AM
10. APHA 1985 *Standard methods for examination of water and wastewater*, p 689-823 16th ed. American Public Health Association, Washington, DC
11. International Organization for Standardization 1982 Water quality: determination of the acute lethal toxicity of substances to a freswater fish (*Brachydanio rerio* (Hamilton-Buchanan), Teleostei, Cyprinidae) Part 1: static method. International Organization for Standardization, Paris (Draft International Standard ISO/DIS 7346/1, ISO/TC 147)
12. Cetesb 1986 *Desenvolvimento de métodos para o estabelecimento de critérios ecotoxicológicos: relatório final 1983*. Companhia de Tecnologia de Saneamento Ambiental, São Paulo
13. International Organization for Standardization 1982 *Water quality: determination of the inhibition of the mobility of* ***Daphnia magna*** *Straus (Cladocera, Crustacea)*. International Organization for Standardization, Paris (Ref. nº 6341-1982 E)
14. Brusik DJ, RR Young 1981 *IERL-RTP-Procedures manual: level 1 Environmental assessment biological tests*. p 53-84 US Envoronmental Protection Agency, Washington, DC (EPA-600/8-81-024)
15. Walsh GE, RG Merrill 1984 Algal bioassay of industrial and energy process effluents, p 329-360 *In Algae as ecological indicators*. L Elliot Shubert, ed., Academic Press, London
16. Zanella EF, SA Berben 1980 Evaluation of methodologies for the determination of acute toxicity in pulp and paper effluents. *TAPPI* 633: 77-82
17. Gherard-Goldstein E, NAGG Fernicola, PA Zagatto, E Bertoletti, RPA Araújo, MCN Moura 1981 *Contribuição da toxicologia ambiental para o controle da poluição*. Cetesb, São Paulo; 11º Congresso Brasileiro de Engenharia Sanitária e Ambiental. Fortaleza, CE
18. Witle DM, KW Flood 1977 Assessment of the acute toxicity, growth impairment and flesh tainting potential of a bleached Kraft mill effluent on rainbow trout (*Salmo gairdneri*) *J Fish Res Board Can* 34: 869-878
19. McLeay DJ 1977 Development of a blood sugar biomassay for rapid measuring stressful of pulp mill effluent to salmonid fish. *J Fish Res Board Can* 34: 477-485
20. Soniassy RN, JC Mueller, CC Walden 1977 The effects of BKME color and toxic constituents on algal growth. *Pulp Paper Can* 78: 179-184
21. Walsh GE, LH Bahner, WB Horning 1980 Toxicity of textile mill effluents to freshwater and estuarine algae, crustacean and fishes. *Environm Pollut (series A)* 21: 169-179
22. Companhia de Tecnologia de Saneamento Ambiental 1982 *Legislação básica: poluição ambiental — estadual e federal*. Companhia de Tecnologia de Saneamento Ambiental, São Paulo
23. Pessah E, GM Cornwall 1980 Use of toxicity tests in regulating the quality of industrial wastes in Canadá, p 130-141 *In Aquatic toxicology*, JG Eaton, PR Parrish, AC Hendricks, eds. American Society fos Testing and Materials, Philadelphia (ASTM STP 707)

24. *Acknowledgement*: The authors particularly wish to thank John B Sprague and Henneth L Dickson for their review and valuable comments.

Received 10 September 1990
Accepted 22 April 1991