

DEGRADATION OF BISPHENOL A IN NATURAL WATERS

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ABSTRACT

In establishing chemical environmental safety, a hazard assessment using environmental exposure and effects information is required. Environmental degradation information is factored into estimates of exposure. The environmental degradation of polycarbonate grade Bisphenol A 2,2'-Bis (p-hydroxyphenyl propane) CAS# 80-05-7, used in the manufacture of plastics, was measured using local waters in the Houston Ship Channel. A spike of 3 mg/L BPA was added to four laboratory units containing fresh water (control). Houston Ship Channel water, Patricks Bayou water (200 yards downstream from a BPA chemical plant discharge), and the chemical plant treated process effluent. Greater than 90% degradation was observed in all treatments except the control within four days. The initiation of biodegradation in the units was in the following order: effluent > Patricks Bayou > Houston Ship Channel.

INTRODUCTION

The hazard evaluation process for evaluating the environmental safety of chemicals requires that not only effects, but exposure must be considered.¹ Often, the most difficult part of the evaluation process is the determination of environmental exposure resulting from discharge or spills of chemicals. It may not be possible to determine chemical fate unless site-specific conditions are present in the experimental test environment. Therefore, data submitted for premarket manufacture notification (PMN) required by the Toxic Substances Control Act (TSCA), may only contain results from screening tests which were designed to provide general information for screening purposes. Refined estimates of environmental effects specifically dealing with site-specific evaluations are not always provided by preliminary or generic data reports for chemicals.

Bisphenol A (BPA, CAS# 80-05-7, Table 1) was proposed for toxicity testing under TSCA section 4.² Data requirements did not include environmental degradation studies although BPA degradation in the environment was stated to require greater than 90 years.² Based on data submitted by manufacturers required in TSCA section 8e, environmental concentrations resulting from treated process effluent discharge would not exceed 0.1 mg/l. However, degradation data using OECD methods for screening chemicals indicated less than 1% degradation in 28 days.³ The study concluded that BPA was not readily biodegradable.

Since the testing was performed using unacclimated systems containing sewage plant seed, adapted cultures utilizing BPA as substrate were unavailable.

(See Table 1)

The aquatic data for BPA showed lowest acute effects (EC_{50}) at approximately 1 mg/l for invertebrates,⁴⁻¹⁰ which was near expected process discharge effluent concentrations (Table 2). To allay fears that an acutely or perhaps a chronically toxic effluent containing BPA was discharged from manufacturing locations, a degradation study using natural receiving waters was initiated.

The objective of the experiment was to: determine the degradation of Bisphenol A (Table 2) under exposures to natural waters in the vicinity of a chemical plant manufacturing BPA located on the Houston Ship Channel.

(See Table 2)

We did not attempt to simulate degradation after a spill, but simulated degradation under exposure to a high effluent concentration of BPA. The highest concentration of BPA expected in effluent was reported to be 0.08 mg/l by Shell,¹¹ in submitting information under TSCA section 8(e), and no greater than 0.1 mg/l on the average by other companies.² The parameters designed into the test were to expose four laboratory units containing: 1) fresh water control, 2) chemical plant treated process effluent, 3) Patricks Bayou water taken 200 yards downstream of the effluent discharge, and 4) Houston Ship Channel. Samples of waters were collected on the morning of December 9, 1985. Approximately 1 gallon of each water was collected by grab sampling in polyethylene cubitainers leaving adequate head space for aeration. Water samples were transported to the Shell Westhollow Research Center in Houston at approximately 20 °C.

The Bisphenol A tested was provided from the Shell Deer Park Chemical Plant resins laboratory (lot #09F11B512). A stock solution of 300 mg/l BPA was prepared by adding BPA into alkaline water. The pH of the stock was adjusted to pH 8.7 with NaOH. A dose of 3.0 mg/l was spiked into each of the water samples for the biodegradation test.

Four 3.785L (1 gallon) glass columns with bottom air inlets were employed for the biodegradability test. The experimental columns were placed within a negative air flow hood under fluorescent light maintained at 8:16 hours light:dark cycle. Deionized water and the three water samples were immediately put into the glass columns and spiked with 3.0 mg/l BPA. The pH was adjusted in each of the four reactors between 7.5-7.7. Each of the water columns were then covered with glass dishes and slightly aerated at a rate of about 0.5 liter per hour.

The pH of the three field water columns were kept between 7.3 and 8.3 and the control was between 6.0 and 8.1. The temperature was 22-25 °C during the test period. Samples of approximately 100 ml were taken from each of the four columns daily and filtered through 0.45-micron pores to remove bacteria, then were refrigerated prior to BPA analysis.

The quantitation of BPA in water samples was done by reverse phase HPLC. A Spectra Physics 8700 Solvent Delivery System and a Waters Associates 441 absorbance detector

with an extended wavelength module were used. A 15-cm ODS-II column was packed with 3 µm Spherisorb particles from Custom LC, Inc. Dual channel UV absorbance were detected at 214 and 229 nm. The detection limit was 0.1 mg/l for BPA.

RESULTS AND DISCUSSION

The three field water samples were analyzed for TOC, COD, alkalinity, ammonia, TKN, Cl⁻, and conductivity as shown in Table 3. The water samples were similar in inorganic parameters. However, the Houston Ship Channel water sample had much lower organic carbon content and COD than the chemical plant treated process effluent and the bayou water. They all appeared slightly turbid and presumably contained sufficient microbes as the seed for biodegradation.

(See Table 3)

The fate of BPA in the four water columns is summarized in Figure 1 and Table 4. The control unit shows no change of BPA concentration within experimental error during the 8-day test, indicating that there was no loss due to air stripping, adsorption, photodegradation, etc., in the laboratory condition. Therefore, the disappearance of BPA in the other three water columns were attributed to biodegradation. Evidence of BPA degradation began after two days in chemical plant treated process effluent and the bayou water. About 15-25% of BPA disappeared from the two columns during the first 48 hours. Sharp reduction of BPA occurred in all three waters in the following two days. On the fourth day, BPA was reduced below detection limit (0.1 mg/l). It is interesting to note the sequential response of the three field water samples on BPA degradation. The duration of the "lag phase" seems to reflect either the distance from a source to BPA (from chemical plant treated process effluent), or the probable level of microbes in the waters spiked with BPA. The effluent sample might have had the highest number of microbes that had been exposed to BPA among the three field waters and was the first to respond. In all waters, BPA disappeared quickly as soon as the systems became acclimated. The pattern of responses did not support the possible physical adsorption of BPA onto suspended solids in the field samples. The acclimation took about 1-4 days.

(See Table 4)

An OECD "Ready Biodegradability" test on BPA was conducted by the Shell Sittingbourne Research Center, United Kingdom in 1983.³ BPA was not oxidized in either the Closed Bottle Test or the Modified Sturm Test.³ Since the seeds used in both tests were obtained from domestic sewage treatment plants, they might not have been exposed to BPA and lacked the capability to degrade BPA. On the other hand, BPA is known to be biodegradable in biotreaters of chemical plants where BPA was manufactured or used. In our study BPA was "readily biodegradable" in waters taken downstream of the chemical plant effluent discharge. Therefore, we believe that any residual BPA from a chemical plant can be biodegraded in the aquatic environment in days instead of years as suggested by EPA.² Estimates of environmental degradation for hazard evaluation and chemical environmental safety should utilize experimental data that simulates environmental conditions to estimate actual exposures. Conservative data

such as that obtained in screening tests (ie, OECD) should be used cautiously for making environmental estimates.

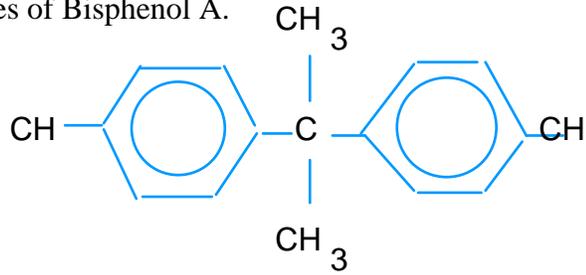
When comparing the chemical structure of BPA with other biodegradable alkylaromatics, it appears that BPA has several potential points of entry for oxygen. Normally, the presence of an alkyl substituent on the aromatic ring presents microorganisms with two alternatives in terms of oxidative degradation. For BPA, oxidative attack on either one of the phenolic moieties would probably lead to the formation of an alkylcatechol which may undergo further ring fission. Organic acids common to intermediate metabolic pathways are usually formed as a result of ring fusion of aromatics. Alternatively, if the methyl group(s) on the propane moiety on BPA is(are) oxidized, alcohol and carboxylic acid derivatives may also be formed. Some alkylbenzenes such as ethylbenzene and isopropylbenzene have been rather extensively studied and shown to be degraded by microorganisms (e.g. pseudomonads) via either or both of the two aforementioned alternative routes.¹² Further biodegradation study on BPA may differentiate if BPA can be ultimately degraded or partially cooxidized by microorganisms.

CONCLUSION

The experimental data strongly suggests that Bisphenol A is biodegradable in the water body receiving a continuous discharge from a BPA manufacturing plant and in the surrounding receiving-waters in the vicinity of the Houston Ship Channel. Since most of the BPA has been shown to be biodegraded in chemical plant biotreaters, our results support that any residual BPA in effluents from chemical plants will be further degraded by microorganisms to non-detectable level in downstream waters.

Table 1. Physical and Chemical Properties of Bisphenol A.

2-2'-Bis (p-hydroxyphenyl) propane

STRUCTUREProperty

CAS #	80-05-7
Molecular weight	228
Aqueous solubility (25°C)	120 mg/l
Melting point (°C)	153-157°
Bulk density (lb/ft ³)	35-41
Vapor pressure (mmHg 170°C)	0.2
Freezing point (°C)	-156.5
Log octanol-water partition (exp.)	2.20
coefficient (log k_{ow}) (calc.)	3.84
Specific gravity (25°C)	1.195

Table 2. Aquatic Toxicology Data Summary (EC/LC₅₀ in mg/l) From References [5-10].

	Freshwater species	Seawater species
Algae	2.7 ¹ , 3.1 ² <u>Selenastrum capricornutum</u>	1.0 ¹ , 1.8 ³ <u>Skelatonoma costatum</u>
Invertebrates	15.5 ⁴ , 10.2 ⁵ <u>Daphnia magna</u>	1.1 ⁶ <u>Mysidopsis bahia</u>
Fish	4.7 ⁷ , 4.6 ⁶ <u>Pimephales promelas</u>	9.4 ⁵ <u>Menidia menidia</u>

1) cell count	5) 48-h static
2) total cell volume	6) 96-h flow through
3) chlorophyll <i>a</i>	7) 96-h static
4) 24-h static	

Table 3. Physical and Chemical Characteristics of Test Water Samples.

	Analysis mg/l except pH and conductivity		
	<u>Effluent</u>	<u>Patricks Bayou</u>	<u>Houston Ship Channel</u>
Appearance	Slightly turbid, light colored	Slightly turbid, light colored	Slightly turbid, light colored
pH	7.5	7.4	7.8
Chemical Oxygen Demand (Ag ₂ SO ₄ + HgSO Method)	123	123	36
Total Organic Carbon	31	35	12
As Calcium Carbonate, CaCO ₃ :			
Total Alkalinity	244	288	116
Total Hardness	1,200	1,300	1,550
Ammonia Nitrogen, N	0.5	1.3	0.73
Kjeldahl Nitrogen, N	2.0	4.5	1.1
Conductivity (µmhos/cm)	7,000	8,200	10,500
Chloride	2,800	4,000	5,000

Table 4. Analytical Verification of BPA in Reactors (mg/l).

<u>Day</u>	<u>Control</u>	<u>Effluent</u>	<u>Patricks Bayou</u>	<u>Ship Channel</u>
0	3.1	2.7	3.0	3.0
1	3.1	2.8	3.0	3.1
2	3.1	1.9	2.5	2.9
3	3.0	1.1	<0.1	2.9
4	-	-	-	-
5	3.0	<0.1	<0.1	<0.1
6	3.1	<0.1	-	<0.1
7	3.0	-	-	-
8	3.0	<0.1	<0.1	<0.1

REFERENCES

1. Cairns, J., K.L. Dickson and A.W. Maki. 1978. Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM Special Technical Publication 657. American Society for Testing and Materials, Philadelphia, PA. 278 pp.
2. EPA. 1985. Bisphenol A: Proposed Test Rule. Federal Register 50(96): 20691-20703, May 17, 1985.
3. Stone, C.M. and R.J. Watkinson. 1983. Diphenylol propane: an assessment of ready biodegradability, SBGR.83.425, Shell Research Limited, Sittingbourne Research Center, Sittingbourne, United Kingdom.
4. Alexander, H.C., D.C. Dill, D.P. Milazzo, and G.U. Boggs. 1985. Bisphenol A: Algal toxicity test, Dow Chemical U.S.A., Midland, MI.
5. Alexander, H.C., D.P. Milazzo, and G.U. Boggs. 1985. Bisphenol A: Daphnid static acute toxicity test, Dow Chemical U.S.A., Midland, MI.
6. Alexander, H.C., E.A. Bartlett, and G.U. Boggs. 1985. Bisphenol A: Flow-through acute toxicity to the fathead minnow, Dow Chemical U.S.A., Midland, MI.
7. Springborn Bionomics. 1985a. Acute toxicity of Bisphenol A to Atlantic silverside (Menidia menidia) under flow-through conditions, Report #BW-85-6-1802.
8. Springborn Bionomics. 1985b. Acute toxicity of Bisphenol A to the marine algae (Skeletonema costatum), Report #BW-85-8-1829.
9. Springborn Bionomics. 1985c. Acute toxicity of Bisphenol A to the mysid (Mysidopsis bahia) under flow-through conditions, Report #BW-85-8-1825.
10. Springborn Bionomics. 1985d. Detection and measurement of Bisphenol A in toxicity tests with saltwater organisms, Report #BW-85-8-1832.
11. Shell Oil Company. Health Saety and Environmental Studies on Bisphenol A. Letter from G.T. Youngblood to Philip Wirdzik, USEPA-OPTS, August 23, 1984.
12. Gibson, G.T. 1984. Microbial Degradation of Organic Compounds. Marcel Dekker, Inc., New York. 535 pp.