

IS WATCHING TELEVISION TOXIC? BFRIP-SPONSORED STUDY ON THE EMISSION OF
PBDD/PBDFS FROM OPERATING TELEVISION SETS

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ABSTRACT

Analysis of the atmosphere surrounding operating television sets showed that no polybrominated dibenzodioxins (PBDDs) and no polybrominated dibenzofurans (PBDFs) are emitted under normal operating conditions.

KEYWORDS

brominated dibenzofurans; brominated dibenzodioxins; decabromodiphenyl oxide

INTRODUCTION

In early 1989, the German magazine Stern published an article entitled "Is Watching Television Toxic?"¹ The article detailed the results of a study commissioned by Stern and the Hamburg environmental authorities to analyze the atmosphere surrounding an operating television set for trace amounts of polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs). According to a test performed by the Hamburg Office for Environmental Testing and the Hamburg Research Society, "Several PBDFs escape from a television set including extremely hazardous 2,3,7,8-tetrabromodibenzofuran (TBDF)". Stern reported measured TBDF concentrations of 11pg/m³ in the air at the rear wall of the television set and 2.7pg/m³ in the air at a distance of 2.2 meters from the set.

These results were accompanied with the admonition for the German governmental authorities to immediately remove the suspected source of the "ultra-toxins", brominated diphenyloxides, from the marketplace. Stern, however, misreported the data. The analyst found no 2,3,7,8-TBDF and the reported concentrations were of total tetrabromodibenzofurans.² The experiment itself suffered from the deficiencies that no samples were taken to determine background PBDF levels, no standards were used to quantitate specific PBDD/PBDF isomers and, possibly, no precautions were used to exclude interfering brominated diphenyloxides during the mass spectral analyses. The latter is particularly important since the brominated diphenyloxides can eliminate two Br atoms during mass spectral analysis to form an ion of the same elemental composition as a brominated dibenzofuran.

The Brominated Flame Retardant Industry Panel (BFRIP) sought to correct these deficiencies by conducting an air monitoring experiment in a controlled environment and analyzing the air samples for specific 2,3,7,8-PBDD/PBDF congeners and total PBDD/PBDFs. Ethyl Corporation, Great Lakes Chemical Corporation and Dead Sea Bromine constitute the BFRIP membership. Ethyl Corporation had responsibility for the experiment.

EXPERIMENTAL

A 1.81 m³ test chamber was constructed from 1.22 x 1.22m polymethylmethacrylate panels which were secured with glue and screws to give an air tight enclosure. A removable front panel, attached with screws and sealed with tape, allowed access to the interior for the introduction of the test items, sampling devices, etc. About 17m³ of air was drawn into the chamber through two 22mm inlet ports fitted with high volume Anderson PUF sampling heads³ which consisted of a 102mm glass fiber filter followed by a glass cartridge containing two polyurethane foam (PUF) plugs. The inlet ports were located on each side of the chamber, 12.7cm from the bottom and 30.5cm from the front panel. Air was drawn out of the chamber through a Dioxin/Furan Sampler designed by Clayton Environmental Consultants.⁴ The sampler consisted of an open face, all Teflon filter holder containing a 47mm glass fiber filter. The filter holder was connected to a glass cartridge which contained 30/70 mesh silica gel spiked with 1000pg of ¹³C₁₂-2,3,4,7,8-PeBDF. The sampler was suspended in the chamber using Teflon tubing attached to a bulkhead fitting in the top panel. Air exited the chamber through a rotameter, through the inlet side of a GAST oil-less piston type pressure/vacuum pump and through a Singer gas meter which measured the total volume of air pulled through the Clayton air sampler. Three new television sets were used for the experiment. Sets A and B were purchased locally while set C was provided by the manufacturer. The rear portion of each television set cabinet was determined by infrared spectroscopy to be constructed of polystyrene. A bromine content of 11.5% suggested that the purchased models were flame retarded with decabromo-

diphenyloxyde. Set C was known to be made of high impact polystyrene flame retarded with decabromodiphenyloxyde/antimony oxide.

Analysis of the air samplers for PBDD/PBDFs was performed by Triangle Laboratories, Inc., Research Triangle Park, North Carolina.⁵ The silica gel and the glass fiber filter paper from a sampler were spiked with $^{13}\text{C}_{12}$ -labeled 2,3,7,8-PBDF standards, extracted with toluene, the extract concentrated, and chromatographed on activated charcoal (20%)/Celite using methylene chloride/hexane followed by hexane/benzene. Elution in the reverse direction with toluene gave the PBDD/PBDFs. The toluene eluant was concentrated, spiked with $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxC1DD recovery standard and analyzed by GC/MS operating in the SIM mode. Channels for PBDDs, PBDFs, and polybrominated-diphenyloxydes were monitored to be certain of identifications.

RESULTS AND CONCLUSIONS

In order to determine background levels of PBDD/PBDFs, air was pulled through the empty chamber and through a sampler for 3 days, eight hours per day. No PBDD/PBDFs were detected. The air sampler was replaced and the two purchased television sets placed in the test chamber. Air was again pulled through the chamber for 3 days, eight hours per day. No PBDD/PBDFs were detected. The experiment was repeated with a new sampler and with the television sets in operation during the three day, eight hour per day monitoring (17.95m^3 of air). Again, no PBDD/PBDFs were found on the air samplers.

The concluding portion of the air monitoring experiment involved the use of the television set whose cabinet was manufactured from HIPS/Decabromodiphenyloxyde/ Sb_2O_3 resins composited from three different suppliers. The two purchased sets were removed from the chamber and the inside of the chamber cleaned with detergent/water. New inlet filters were installed as well as a new Dioxin/Furan sampler. The television set was placed in the chamber and air monitoring was conducted for 3 days, eight hours per day with the set not operating. No PBDD/PBDFs were found. The sampler was replaced and the air (15.11m^3) was monitored for 24 continuous hours while the television set was operating. Again, no PBDD/PBDFs were found.

The two separate experiments with the environmental chamber, one involving two commercial television sets and another using an industry composite, showed that no PBDD/PBDFs are emitted under normal operating conditions. Very low detection limits were observed in these experiments:

	Experiment 1 (Detection Limits)	Experiment 2 (Detection Limits)
2,3,7,8-TBDD	$27.4 \times 10^{-12} \text{g}$	$2.5 \times 10^{-12} \text{g}$
Total TBDD	27.4	2.5
1,2,3,7,8-PeBDD	6.2	5.9
Total PeBDD	6.2	5.9
2,3,7,8-TBDF	6.0	1.3
Total TBDF	6.0	1.3
1,2,3,7,8-PeBDF	3.6	3.7
2,3,4,7,8-PeBDF	2.1	2.2
Total PeBDF	2.6	2.8

Based on these detection limits, PBDD/PBDF emissions from the operating television sets can be calculated to be less than $0.17\text{-}1.53 \text{ pg TBDD/m}^3$, $0.35\text{-}0.39 \text{ pg PeBDD/m}^3$, $0.09\text{-}0.33 \text{ pg TBDF/m}^3$ and $0.14\text{-}0.19 \text{ pg PeBDF/m}^3$ of air. In actual practice, these maximum values would be lower by a factor of 10-100 due to the dilution effect of a normal room size and the expected air turnover.

REFERENCES

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- ³ Anderson Samplers Inc., Atlanta, Georgia
- ⁴ Clayton Environmental Consultants, Southfield, Michigan.
- ⁵ "Analytical Protocol For The Analysis of Polybrominated Dibenzodioxins and Dibenzofurans: Data Quality Objectives and Single-Laboratory Evaluation," Yves Tondeur, R. Gorsich, C. Mazac, J. Hass and D. McAllister, Dioxin '89, Toronto, Canada, September 17-22, 1989.