

AN EXAMINATION OF THE RELATIONSHIP OF AOX CONTENT
IN PAPER INDUSTRY WASTEWATERS TO POTENTIAL BIOLOGICAL EFFECTS

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ABSTRACT:

The AOX concentrations in NCASI's experimental streams studies have been estimated from effluent quality data generated shortly after the studies had concluded. At AOX concentrations in the streams of approximately 1.6 mg/L, no effects on rainbow trout growth or production were found. No effects on the growth or production of any of three southern fish species were observed at AOX concentrations in the streams of approximately 1.8 mg/L.

NCASI has analyzed 26 sets of data where AOX measurements could be paired with *C. dubia* 7-day bioassay test results on biologically-treated wastewaters, and 21 sets of comparable data generated using the fathead minnow 7-day bioassay test. No statistically significant correlations were found at the 0.05 level of significance relating increased concentrations of AOX to decreased survival, growth, or reproduction. Some of the relationships approached statistical significance ($0.1 > \alpha > 0.05$), but in no case did AOX concentrations account for as much as one-third of the variability in bioassay responses ($r^2 < .33$).

INTRODUCTION

Questions about the compatibility of effluents from pulp and paper manufacturing facilities with the distribution and abundance of valuable fish species and the maintenance of a diverse aquatic community have changed in character in recent years. Recent questions have focused on the effects of chlorinated organic compounds in effluents from mills with chlorine bleaching. In only the past 3-4 years the use of adsorbable total organic halides (AOX) has been proposed both as a method of measuring the amount of chlorinated organic compounds in effluents and as a measure of possible adverse effects. AOX is also receiving attention as a parameter for possible regulation in several countries or states (1).

The amounts of AOX being discharged were measured during the 104-mill study in mid-to late - 1988. The mean discharge in biologically-treated wastewaters from 71 chemical pulping mills practicing chlorine bleaching was 2.7 kg AOX/air-dried metric ton of bleached pulp. A recent summary of information on the effects of pulp and paper mill effluents in the aquatic environment has been published (2). A science advisory panel concluded from that information that with the usual treatment and dilution there was little evidence that adverse effects were occurring. The panel also noted that where effects were measured evidence that chlorinated organic compound were causing such effects was not compel-

ling, and further information comparing the chemical quantities in effluents to biological responses would be useful (3).

The recent interest in the effects of AOX on aquatic communities, has led to a few studies which attempt to correlate the amounts of AOX in effluents with biological effects (1). One study by Gergov et.al. found that the amount of AOX was unrelated to the LC₅₀'s of Daphnia magna exposed to bleach stage filtrates from modern and conventional mills pulping birch, pine and hardwood (4). In a second study Hall et.al. measured the concentration AOX in effluents from several bleach plant filtrate stages from three softwood and hardwood pulping mills (5). The LC₅₀'s of these effluents to D. magna were also measured. Although the authors made no direct comparisons, toxicity of the effluents to D. magna appeared to be poorly correlated to the AOX concentration (r^2 calculated by NCASI to be 0.057). In a third study by Firth and Backman (6), the LC₅₀ values for rainbow trout (Oncorhynchus mykiss) were compared to AOX, low molecular weight AOX (mw <1000), and BOD₅. An analysis of data generated on a variety of treated and untreated waste streams at a single bleached kraft mill revealed that low molecular weight AOX was correlated to the trout LC₅₀s ($r^2 = 0.88$). No relationship was found between acute toxicity of final effluents to rainbow trout and AOX or low molecular weight AOX. Further, no significant relationships were found between Microtox or Ceriodaphnia toxicity in final effluents and total phenolic compounds, AOX, or low molecular weight AOX.

This paper contains information generated in NCASI's experimental streams research program and bioassay data generated on treated wastewater samples where concentrations of AOX were known. The measurements of AOX shown in this report were completed at the NCASI West Coast Regional Center. Samples for AOX analysis were collected, preserved, and shipped as described in NCASI technical bulletin 498 (7). The methods used are described in Standard Methods - 16th Edition (8).

AOX IN THE EXPERIMENTAL STREAMS SITES

A. Northern Experimental Streams -- AOX Measurements

AOX was not routinely measured during the analysis of effluent from the Northern Experimental Streams Site. Four measurements of AOX are available for the effluent from the Northern Experimental Streams site shortly after the conclusion of these studies. The mean concentration of AOX from these analyses was slightly greater than 31 mg/L. These numbers may be used as an indication of the AOX present in the final effluent used in studies described in NCASI Technical Bulletin 566, which summarizes studies in the Northern Experimental Streams (9).

The concentration of effluent entering the streams averaged approximately 1 to 5 percent by volume over the years of the study. An estimate of the amount of AOX in the experimental streams can

be calculated by multiplying these average concentrations by the median of the 4 AOX measurements. This results in a range of 0.32 to 1.6 mg/L of AOX in the streams over the time of the studies. The highest average concentration which caused no adverse effect on the growth and production of rainbow trout was 5 percent by volume, and the calculated amount of AOX in the stream was 1.6 mg/L.

B. Southern Experimental Streams – AOX Measurements

Measurement of AOX was not performed routinely measured in the effluent from the Southern Experimental Streams site. Five AOX analyses were available for samples of the effluent collected shortly after the conclusion of these studies, which are described in Reference 10. The concentration of effluent entering the streams averaged approximately 4 to 15 percent by volume over the years of the study. An estimate of the amount of AOX in the experimental streams can be calculated by multiplying these average concentrations by the median of the 5 AOX measurements. This results in a range of 0.72 to 2.7 mg/L of AOX in the streams over the time of the study. The highest average concentration which caused no adverse effect on the growth and production of any fish species was approximately 10 v/v %, and the calculated amount of AOX in the stream was approximately 1.8 mg/L.

RELATIONSHIP OF AOX TO RESULTS OF Ceriodaphnia dubia SEVEN DAY SURVIVAL AND REPRODUCTION TESTS AND SEVEN DAY FATHEAD MINNOW (Pimephales promelas) SURVIVAL AND GROWTH TESTS

Twenty-six pairs of data for C. dubia and twenty-one pairs of data for fathead minnows were available from the data set containing measurements of AOX and acute or chronic end points (11). Data were from a variety of mills and laboratories, although all AOX data were generated by NCASI. The data pairs were usually, but not always from the same effluent sample. A statistically significant correlation suggesting an association of increased toxicity with increased AOX was not found. Regression slope parameters were never significantly different from 0 at the 0.05 level of significance (except on one occasion where increased toxicity was suggested to be associated with lower AOX concentrations). In several instances, the slopes approached statistical significance ($0.1 > \alpha > 0.05$) but in no case did the AOX concentrations explain as much as one-third of the variability in bioassay response ($r^2 < 0.33$).

Efforts to identify the factors affecting bioassay response continue. Additional data may allow the identification of statistically significant relationships between AOX and bioassay response either within individual mills or among mills practicing similar pulping and bleaching techniques. However a statistically significant association between increased AOX concentrations and reduced C. dubia survival and reproduction, or reduced fathead minnow survival and growth cannot be demonstrated from this data set.

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