RAINY RIVER WATER QUALITY IN THE VICINITY OF BLEACHED KRAFT MILLS

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ABSTRACT

Water and suspended solids samples were collected at four river stations and from two pulp and paper mill final effluents and analysed for a variety of organic contaminants. Juvenile fish were collected both above and below the mill discharges. Results showed significant mill inputs of PCBs, PAHs, chlorophenols, dioxins and furans which impacted downstream stations. Juvenile fish analysed downstream of the effluents indicated uptake of PCBs and chlorinated phenols.

INTRODUCTION

The Rainy River forms the international boundary between Ontario (Canada) and Minnesota (United States) linking Rainy Lake and Lake of the Woods. It has a drainage basin of 54,000 km^2, of which, two-thirds lies upstream of the outlet of Rainy Lake. Two bleached kraft mills are operated by the Boise Cascade Corporation at the upstream end of the river in Fort Frances, Ontario and International Falls, Minnesota. The daily average flow of the final effluents during 1988 was 74,600 m^3/day at the Ontario mill compared to 122,666 m^3/day at the Minnesota mill, while the average daily flow for the Rainy River was 248 m^3/s with a maximum daily flow of 892 m^3/s and a minimum daily flow of 51 m^3/s. This study was undertaken to assess the concentration and distribution of a wide variety of organic contaminants in water, suspended solids and juvenile fish.

METHODS

Large volume (38L) centrifuged water and suspended solids samples were collected at four river locations and from the final effluents of the two mills during June and August, 1988. The river sampling sites included one control station upstream of the pulp mills that is not impacted by any other discharges, two sites located downstream of each mill diffuser , and one station located about 5 km downstream of the mill discharges. Juvenile fish, namely yellow perch (Perca flavescens), log perch (Percina caprodes), and smallmouth bass (Micropterus dolomieui) were collected upstream and downstream of the mill discharges during the August survey.

A Westfalia separator was used on site to collect clarified water and suspended solids samples. Large volume samples were extracted in the field using a continuous flow mixer-settler extractor (Goulden and Anthony, 1985) and analysed in the laboratory for organochlorine pesticides, PCBs, chlorobenzenes

and PAHs. Chlorophenols were collected in 4L pre-cleaned amber glass bottles and preserved on site to pH 2 with sulfuric acid. Solids and fish samples were analysed for dioxins and furans in addition to those variables analysed in water. Further details on sampling protocols and analytical methodologies may be found in Environment Canada, 1990; Merriman, 1988; and Wilkinson and Afghan, 1990.

RESULTS AND DISCUSSION

Of the 17 organochlorine pesticides analysed, alpha and gamma-BHC were detected in water below the guideline for the protection of freshwater aquatic life set at 10 ng/L. There was only one solids sample in which alpha-BHC was found above the detection limit and none of the fish samples were above the detection limit of 5 ng/g. TDE, a breakdown product of DDT was found in some solids and fish samples either in the final effluents or downstream of the mill discharges. Concentrations of TDE ranged from a high of 10 ng/g in suspended solids to a high of 14.5 ng/g in fish.

Total PCBs were significantly higher in water samples collected from the Ontario mill effluent with a high of 334 ng/L recorded, in comparison to the Minnesota mill which had a high of 85.6 ng/L. Concentrations upstream of the mills ranged from below the detection limit of 3.3 ng/L to 6.6 ng/L, while at the downstream location a concentration of 325 ng/L was recorded during the August survey. Total PCBs in river samples exceeded freshwater aquatic life guidelines of 1 ng/L for all but 2 samples that were below the detection limit of 3.3 ng/L.

Although suspended solids concentrations of PCBs at the Ontario mill were high (414 ng/g), both the June and August samples at the downstream site were below the detection limit of 77 ng/g. Concentrations of PCBs in solids downstream of the Minnesota diffuser were higher (243 ng/g) during the August survey than what was found in the mill's final effluent (131 ng/g). This may be the result of daily variations in mill effluents and also because the mill and river stations were sampled on different days. Large variations in concentrations at both mills are apparent between the June and August surveys. PCBs in juvenile fish were not found in samples collected upstream of the mill effluents, but were detected in three of four samples downstream, the highest concentration being 229 ng/g.

Chlorobenzenes, namely, 1,2-; 1,3-; 1,4-DCB and 1,2,4-TCB were found in water at concentrations as high as 18.8 ng/L which are well below the freshwater aquatic life guidelines of 2.5, 2.5, 4.0, and 0.5 ug/L, respectively, for the isomers detected. The highest concentrations were found in the final effluents with lower levels downstream, while upstream at the control station, all samples were below the detection limit. No detections of chlorobenzenes were found in either suspended solids or fish samples.

Eleven of sixteen PAHs analysed in large volume water samples were found to be above the detection limit of 0.5 ng/L. By far, the highest concentrations were found in the Minnesota mill effluent where total PAHs ranged from 3,174 to 3,243

and 41.8 ng/L. Total PAHs at the downstream station varied between 103.4 ng/L for the June survey and 89.6 ng/L for the August sampling date.

PAHs in solids showed a similar spatial distribution to that found in the aqueous phase. The upstream station did not have detectable amounts of PAHs, while the highest concentrations were found in the two mill effluents. Decreasing concentrations were evident downstream of the mill effluents. PAHs were found in 4 of 6 juvenile fish samples with concentrations ranging from below the detection limit to a high of 124 ng/g. There was no apparent distribution pattern with detections both above and below the mills. PAHs detected in fish were the lighter molecular weight types with 2 aromatic rings, while those found in solids samples had higher molecular weights with 3 and 4 aromatic rings.

Eleven of twenty chlorinated phenols analysed, were found to be above the detection limit in water samples from the Ontario mill final effluent in comparison to three isomers found at the Minnesota mill. Both 2,4-DCP and 2,4,6-TCP were the most prevalent isomers detected, with concentrations of 2,4,6-TCP as high as 14,776 ng/L at the Ontario mill and decreasing to 104 ng/L at the downstream river station. Concentrations of 2,4-DCP were found as high as 3,996 ng/L at the Ontario mill, while they were undetectable at the downstream site. Chlorophenols were not detected in water samples at the upstream station. None of the chlorophenol water quality guidelines for the protection of aquatic life were exceeded.

The highest chlorophenol concentrations in solids were present at the Ontario and Minnesota mills with decreasing concentrations found downstream of the discharges. Predominant isomers included 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP and PCP. There were also some detections of monochlorophenols. 2,4,6-TCP was detected upstream of the mill discharges at a concentration of 66 ng/g, which was the lowest detectable concentration found in solids samples. Both 2,4-DCP and 2,4,6-TCP were found in juvenile fish in 3 of 4 samples collected downstream of the mill discharges. As was the case for the water samples, no chlorophenols were detected in fish upstream of the mills.

Both dioxins and furans were detected in solids samples throughout the study area. 2,3,7,8-TCDD was highest in the mill effluents with concentrations ranging fron 114 to 252 pg/g. Downstream of the discharges, concentrations decreased and were lowest (54 pg/g) at the furthest downstream site. There were no detections of 2,3,7,8-TCDD upstream of the mills. HpCDD and OCDD were found to be widespread in the study area. Concentrations of HpCDD were below the detection limit in both mill discharges on two occaisions, yet were detected upstream of the discharges at concentrations of 93 and 70 pg/g. Downstream, higher concentrations up to 580 pg/g were recorded. OCDD was found at all stations with concentrations ranging from 117 to 1,864 pg/g. Lower levels were recorded at the upstream sites, while the highest concentrations were found downstream of the mill discharges as was the case with HpCDD. HpCDD was detected at a concentration of 122 pg/g in the log perch sample collected downstream on

the Minnesota side of the river. No other detections of dioxins occurred in juvenile fish.

High levels of 2,3,7,8-TCDF were found in solids samples from the mill final effluents, with concentrations ranging from 497 and 542 pg/g at the Ontario mill to 698 and 2,389 pg/g recorded at the Minnesota mill. No detectable quantities were found upstream. There were no apparent spatial distributions for other furan congener groups. Detections of PeCDF, HxCDF, HpCDF and OCDF ranged in concentrations up to 779 pg/g and were primarily found either in the mill effluents or downstream. Furans were not detected in any of the juvenile fish samples.

The Ontario and Minnesota mills are presently implementing abatement measures and process changes to reduce the formation and discharge of chlorinated organics. Both mills will employ chlorine dioxide substitution by 1991 ranging from 50% to 70% at the Ontario mill, to 50% at the Minnesota mill, with the expectation that chlorinated organics will be significantly reduced. Other process changes include condensate stripping at both mills and improved brownstock washing at the Minnesota mill. In 1993 the Minnesota plant will convert from a softwood/hardwood feedstock to a 100% hardwood feedstock which will further reduce chlorinated organic formation and discharge.

In summary variables analysed were for the most part below analytical detection limits upstream of the mill discharges. Those that were detected were much lower than what were found in the mill effluents and usually lower than concentrations found in the Rainy River downstream of the discharges. The mill discharges were characterized by PCBs in both aqueous and solid phase with higher concentrations found at the Ontario mill. PAHs were highest at the Minnesota mill in both water and solids. Chlorophenols were highest in water samples from the Ontario mill, while high concentrations in solids were evident from both effluents. Both 2,3,7,8-TCDD and 2,3,7,8-TCDF were discharged in solids from the mills. Downstream of the discharges, elevated levels of PCBs, PAHs, chlorophenols, dioxins and furans in comparison to the upstream station were found, indicating the impact of the mills. Juvenile fish showed uptake of PCBs and chlorophenols downstream of the mills.

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