

## PCDD, PCDF and PAH Identification at Powell River B.C.

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### Introduction

PCDDs, PCDFs and PAHs are formed as the products of incomplete combustion in coastal pulp mill operations, where salt-laden bark from ocean floated logs is burned in recovery boilers (1). A Canadian survey into levels of PCDDs and PCDFs and PAHs at locations across Canada provided an opportunity to assess a fingerprinting technique to develop source-receptor relationships.

### Material and Methods

Sampling was performed with high volume - polyurethane foam samplers (HV-PUF) with a higher volume flow controller and motor to collect sufficiently large air volumes for sample analyses in the picogram (pg) levels. The sampler was located one kilometer south-east of the mill area during the program. Efforts were made to ensure there was no local source of combustion products that could affect the results of the sampling program. Sampling started September 1996 and is on-going. Samples were taken on a cycle of every twelfth day for PAHs and every twenty-fourth day for PCDDs, PCDFs and PAHs. Analyses were performed by gas chromatography - mass spectrometry using selective ion measurement techniques at the federal laboratory in Ottawa. Quality assurance results were well within limits for precision and accuracy (2).

### Results and Discussion

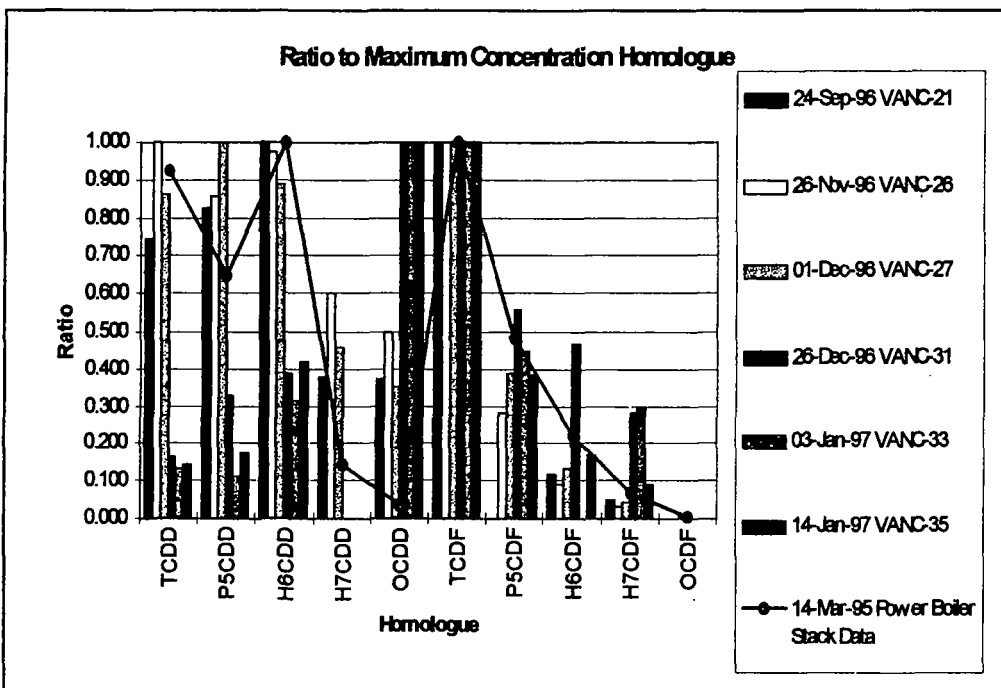
The limited sampling frequency has provided limited data. The congener data were also evaluated in terms of the toxic equivalency factors (TEFs). PCDD and PCDF concentrations ranged from 6-67 fg TEQ/m<sup>3</sup> or 0.44-2.53 pg/m<sup>3</sup> total PCDDs and PCDFs and were similar to that in other urban sites (10-80 fg TEQ/m<sup>3</sup>), but nowhere near the values measured for sites near industrial point sources (10-400 fg TEQ/m<sup>3</sup>) (2). Total congener results varied from 0.17 - 3.94 pg/m<sup>3</sup>. Total homologue results varied from 0.77-5.53 pg/m<sup>3</sup>. In terms of TEQ, congener data gave a variation from about 5.5 to 67.1 femtograms TEQ per cubic meter (fg TEQ/m<sup>3</sup>) over the sampling period.

The Powell River mill was sampled for emissions from both power boiler and recovery boiler systems by the British Columbia Ministry of Environment, Lands and Parks (MoELP) (3).

A technique used to fingerprint the PCDDs and PCDFs concentrations by creating ratios was used (4) to assess different sources of PCDDs and PCDFs. In this approach, homologue groups, which represents the total of all the PCDD and PCDF congeners in the sample, were normalized to the most abundant homologue found. The congener data (and corresponding TEQ data) are a subset of this homologue data and give a similar chemical pattern distribution. Assuming the source operate in a constant manner, then the ambient emissions should have a consistent concentration pattern. Production of PCDDs and PCDFs from combustion sources is highly dependent on combustion material, temperature and moisture values. Changes in these could provide some variation in the amount and distribution of the combustion processes. A normalized ratio of chemicals within chemical groups should reduce the amplitude noise in sample comparisons and provide an analysis tool. However, other factors that could influence this ratio technique could be due to meteorological changes such as wind direction, wind speed and precipitation.

The "normalized homologue data (Figure 1) shows a similar distribution to the mill boiler data, significant agreement for the PCDF homologues and general agreement for the PCDD congeners. PCDD ratio patterns are not as consistent as those for the PCDFs. For the first few samples there appears to be good correlation with the mill boiler profile, but this changes with subsequent samples which have a different profile than the first set, possibly due to a change in mill operations over the Christmas and New Year periods.

Figure 1: Ratio to maximum homologue concentration

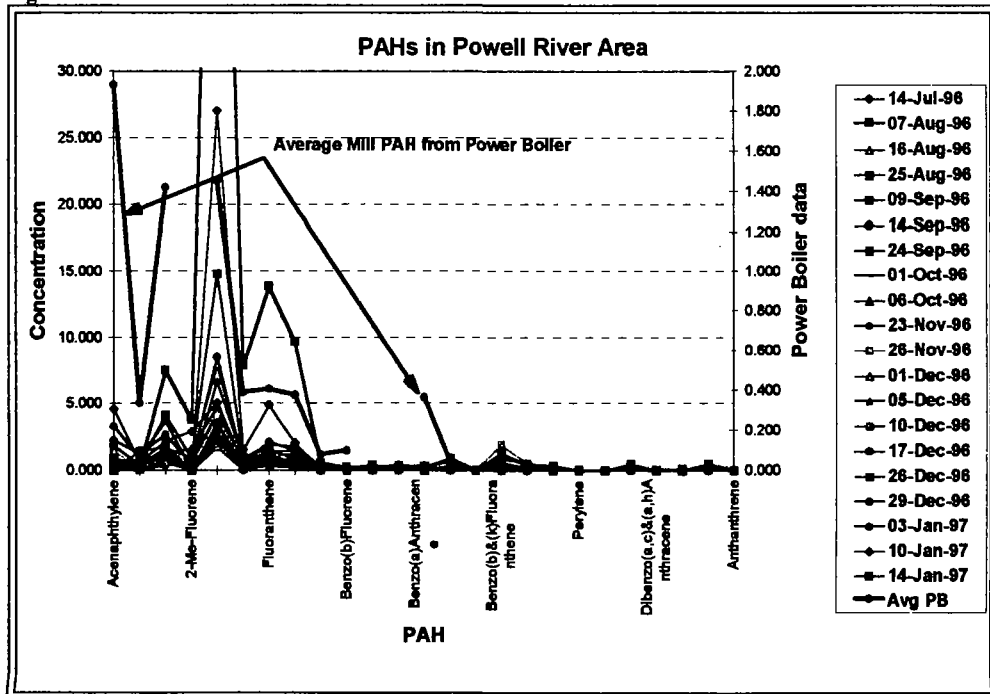


Similar ratios were developed for the congener and the TEQ data values. There is good agreement between mill and ambient data for the PCDDs profile, and similar but lower agreement for the PCDF profile. The TEQ data appears to have the best fingerprint relationship between the mill and ambient data.

The 25 PAHs considered in this assessment were a standard group of non-oxidized, non-nitrated and non-hydrated PAHs. Results for total PAHs vary from 3.7 to 125 ng/m<sup>3</sup>. Data from other areas report a mean concentration of 56 ng/m<sup>3</sup> total PAHs in Columbia SC (5) and 93 ng/m<sup>3</sup> in Denver CO (6). Total PAH data in measurements across Canada (2) have had concentrations of 0.1-9 ng/m<sup>3</sup> in remote areas, 1-11 ng/m<sup>3</sup> in rural areas, 12-100 ng/m<sup>3</sup> in urban areas and 10 to >1000 ng/m<sup>3</sup> from point source impacts. Concentrations in Powell River do not appear to be unusually high for an urban/ point source impact location.

The most commonly found PAHs were of the lower molecular weight type: phenanthrene, fluoranthene, pyrene and anthracene. Distribution patterns were similar throughout the sampling period (Figure 2). Five PAHs with toxic equivalency factors were evaluated for their potential toxicity. Results for these five PAHs vary from 0.005-0.619 ng B(a)P TEQ/m<sup>3</sup>. The Federal German government has proposed a guideline limit (7) of 10 ng/m<sup>3</sup> for annual B(a)P concentrations - well above local measurements in Powell River.

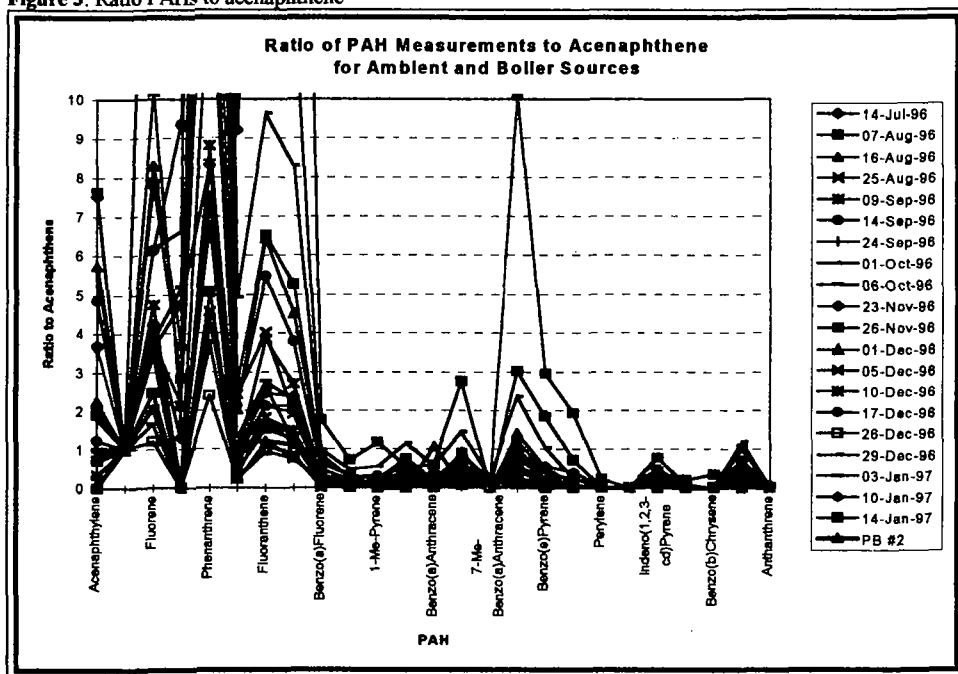
Figure 2: PAHs in Powell River



The B.C. MoELP data set for boiler emissions (3) included measurements on a large number of the PAHs in the federal data set. The data for the PB and the RB systems had very similar distributions in weight concentrations. This data was compared with ambient air data.

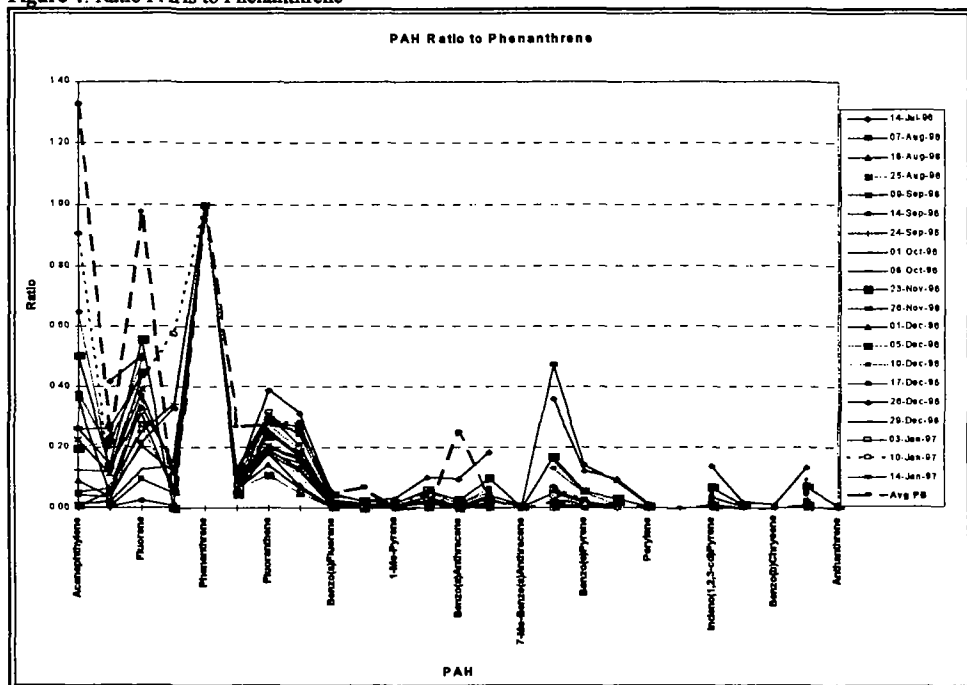
Combustion-type PAHs with 5-member rings are typically linear and kinetically unstable compared to thermodynamically stable petrogenic PAHs with 6-member rings. When the primary PAH source is combustion, the less stable kinetic PAH isomers tend to be enhanced relative to the more thermodynamically stable PAHs. This type of PAH distribution is what has been observed in the data obtained in this sampling program. A PAH ratio technique to assess sources was used by researchers (8) to determine possible PAH sources. When the ratio of kinetic to thermodynamic isomers is predominantly kinetic, this indicates anthropogenic sources. This ratio, along with the presence of known combustion-specific PAHs (acenaphthene and acenaphthylene) can be used to identify anthropogenic sources. Yunker (8) recommended using the ratios of a number of PAHs of different molecular mass. Data in Figure 2 for all PAH compounds showed that similar concentration peaks exist for several of the PAH compounds (acenaphthalene, fluorene, phenanthrene and fluoranthene). For a ratio of PAHs to a specific PAH, such as acenaphthene and phenanthrene, the comparison of the ambient and boiler data (Figure 3 and Figure 4) was made.

Figure 3: Ratio PAHs to acenaphthene



These ratios show agreement for the light molecular weight compounds (<178). Individual ratios of congeners for indeno(1,2,3-cd)pyrene/ (indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene) and fluoranthene/ (fluoranthene + pyrene) are about 0.6 and 0.5 respectively, which are similar to those measured in arctic aerosols (9). Clearly the data in the air samples indicates combustion sources. The fact that these ratios are similar for both ambient air and boiler gas samples tends to enforce the theory that the air concentrations have a likely source from the mill boiler.

Figure 4: Ratio PAHs to Phenanthrene



PAH data was in the range 4-125 ng/m<sup>3</sup> and were comparable to PAH concentrations in other urban areas in Canada, but nowhere near the values measured for sites near industrial point sources (10<sup>1</sup>-10<sup>3</sup> ng/m<sup>3</sup>).

Using ratio techniques to make data more comparable appears to work for PCDDs and PCDFs. The ratios for homologues, congeners and toxic equivalent values all appear to have some value in fingerprinting a source-receptor relationship. The ratios for the TEQ values appear to have the most agreement, even though they do not represent the total amount of PCDDs and PCDFs in the sampled atmosphere. The data ratios for PCDD and PCDF data for ambient air when compared to mill emission data implies that the mill is the source of these ambient air contaminants in the Powell River area. Similarly, the concentration comparisons for PAH data in the ambient air and from mill sources re-enforces the implication that the mill is the primary source of PAH air contaminants in the Powell River area. The continued sampling program

should provide more data to identify which fingerprinting technique is the most appropriate in assessing the source-receptor relationship.

The most likely source of the PCDDs, PCDFs and some PAHs appears to be from the boiler emissions at the local pulp and paper mill. Because of the toxic nature of these compounds and the need for elimination from the environment under CEPA legislation, the ambient concentration levels should continue to be monitored. The impact of these emissions is unknown, and a more detailed study is necessary to assess the total deposition to the area and to determine all sources of these chemicals.

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