Polycyclic Aromatic Hydrocarbons in Water, Fish and Deer Liver Samples Following Forest Fires

Stephan Gabos[1], Donald Schopflocher[1], Brian R. Fowler[2], Jay White[3], Ellie Prepas[3], Dennis Prince[4], Weiping Chen [1]

[1] Alberta Health, P.O. Box 1360, 10025 Jasper Ave. Edmonton, AB, Canada, T5J 2N3 [2]Axys Analytical Services Ltd., Sidney, BC, Canada, V8L 3S8, [3] Sustainable Forest Management Network, Edmonton, Canada, T6G 2E9 [4] Water West Consulting, Edmonton, Canada

Introduction

The warm and dry winter conditions in the Boreal Plain ecozone of western Canada following El Niño in 1997-1998, and the high occurrence of older, more fire-susceptible forest stands in this region, were important factors behind the above-average fire activity in north-central Alberta during the summer of 1998. These fast moving fires were among the most extensive ever recorded in North America. In Alberta alone, over 350 000 hectares of forest were burnt in over 50 separate fires. The largest and most extensively burned one was in the Virginia Hill area, Northern Alberta. In the fall of 1998, a pilot study was conducted to examine persistent organic pollutants following forest fires. The purpose of this study is to examine PAH loading in water, fish and deer liver tissue in the Virginia Hill area and its surrounding area, Alberta, Canada.

Materials and Methods

Sampling

Field collection was carried out at three selected sites in September 1998. Site A (54^{o} 26.989 N, 116^{o} 07.590 W) was located on a reach of the Sakwatamau River which ran through the forest fire area. This site was in a partially burned area on the edge of the forest fire zone. Site B (54^{o} 35.659 N, 115^{o} 39.694 W) was a completely burned area near the middle of the forest fire zone on the Freeman River. Site C (54^{o} 15.536 N, 117^{o} 06.458 W) was on the Little Smoke River in an area that had not experienced forest fires during the year. Three water samples (4 liters per sample) and one field blank sample were collected in solvent-washed glass bottles from each site. Two arctic grayling (weight of 40 grams) and three mountain whitefish (weight of 40 to 100 grams) were collected at Site A and Site C, respectively. Between November and December 1998, five deer liver samples were collected in Virginia Hill and five samples were collected from the Swan Hills area (roughly 30 to 100 km east of Virginia Hill). All samples were kept frozen at -20 ^{o}C prior to laboratory analysis.

Chemical Analysis

Analysis was performed by Axys Analytical Services Ltd. in Sidney, British Columbia, Canada. A total of 18 parent and 30 alkyl PAH series of some parent PAHs were analyzed in all samples from all sites. A total of 62 non-routine PAHs were analyzed in one sample from each site. The sample (approximately 6 to 7 grams dry weight) is spiked with a suite of deuterium labeled PAH surrogate standards, ground with anhydrous sodium sulfate, packed into a column and eluted with methanol followed by dichloromethane. The extract was fractionated and transferred onto a silica gel column. The elute was extracted by column chromatograph on silica

gel into a polar PAH and a non-polar (alkane) fractions. The polar fraction was analyzed by gas chromatograph/mass spectrometry (GC/MS). Extract was analyzed using Finnigan MAT INCOS 50 Mass Spectrometers, each equipped with a Varian 3400 gas chromatograph, a CTC A200S autosampler and a Prolab data system. The sample detection limits (the lowest quality of each compound can be measured in each sample) were used. Quality assurance and quality control were monitored on a batch basis by analysis of method blank, a spiked blank and sample duplicate every batch of 8 samples.

Results and Discussion

Naphthalene and its alkyl derivatives, acenaphthylene and phenanthrene were detected in surface water over a range from 0.7 to 17 ng/L (Figure 1). The concentrations of these PAHs were lower in surface water as compared to other studies.[1] Major sources of PAHs in surface water come from deposition of atmospheric PAHs, industrial activities and natural events.[2] PAHs tend to be removed from the water column quickly through different transport and degradation processes. An important PAH degradation process in water is photooxidation. Photolysis of naphthalene is slower than that of other PAH compounds.[3] The higher water-soluble naphthalene and resistance to photolysis may account for presence of these PAHs in water.

Several lower molecular weight PAHs were detected in five fish at low concentrations (<8 ng/g, wet weight) (Figure 2). Arctic grayling and mountain whitefish are sediment-associated fish species. These fish can uptake PAHs from water, sediment and invertebrates. The PAH levels in fish are usually low because they are readily metabolized and excreted.[4] Particularly, high molecular weight PAHs do not tend to accumulate in fish.[5] The average levels of PAHs in aquatic organisms, especially marine organisms, from various studies ranged from 1 to 100 ng/g.[1,6] Little information on background PAH levels for these two freshwater fish species is available.

Eleven parent PAH compounds were detected in deer liver samples. Mean levels of total PAH (sum of 11 compounds) were higher in samples from the Swan Hills area (267 ng/g, lipid weight) than those from the Virginia Hill (36 ng/g, lipid weight) ($p=0.06$, two non-parametric tests). Figure 3 shows a biplot of the first two components from a principal component analysis of the data. The chemicals are plotted according to their loading on the two components, while the individual samples are plotted according to their component scores on these factors. The chemicals fall into two main groups, while the majority of the individual samples fall near the origin. Two samples, both from the Swan Hills study region show high values. Lines are drawn in Figure 3 from these outliers to the origin. One of the outliers is very high relative to other samples on the larger group of chemicals (including naphthalene) and low on the other group, while the other outlier shows high values on the second group of chemicals (including Dibenzo[ah]anthracene) with low values on the first group of chemicals. The information on background levels of PAHs in deer is limited. Different patterns of parent PAHs in deer liver samples between two areas may indicate different exposure sources. A special waste treatment center is located in the Swan Hills area. Also, there are activities related to oil exploration and production in the entire Virginia Hill and Swan Hills areas.

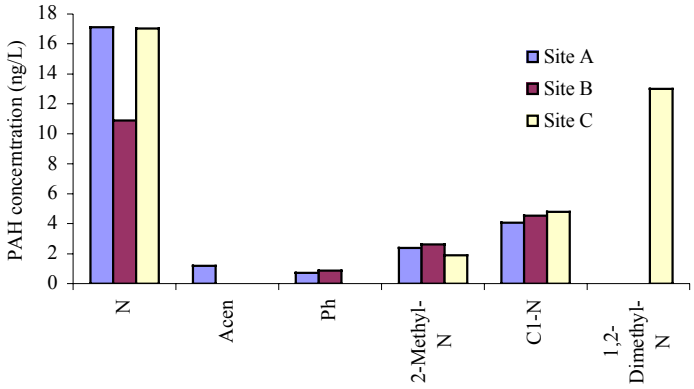

Figure 1 Distribution patterns of parent PAHs and alkyl PAHs compounds in water. N is naphthalene, Acen is acenaphthylene, Ph is phenanthrene.

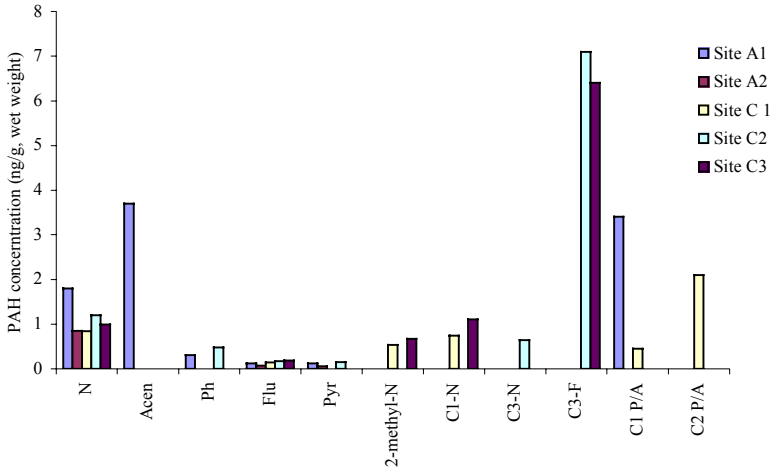

Figure 2 Distribution patterns of PAH compounds in fish. N is naphthalene, Acen is acenaphthylene, Ph is phenanthrene, Flu is Fluoranthene, Pyr is pyrene, F is fluorene, and P/A are phenanthrenes/anthracenes.

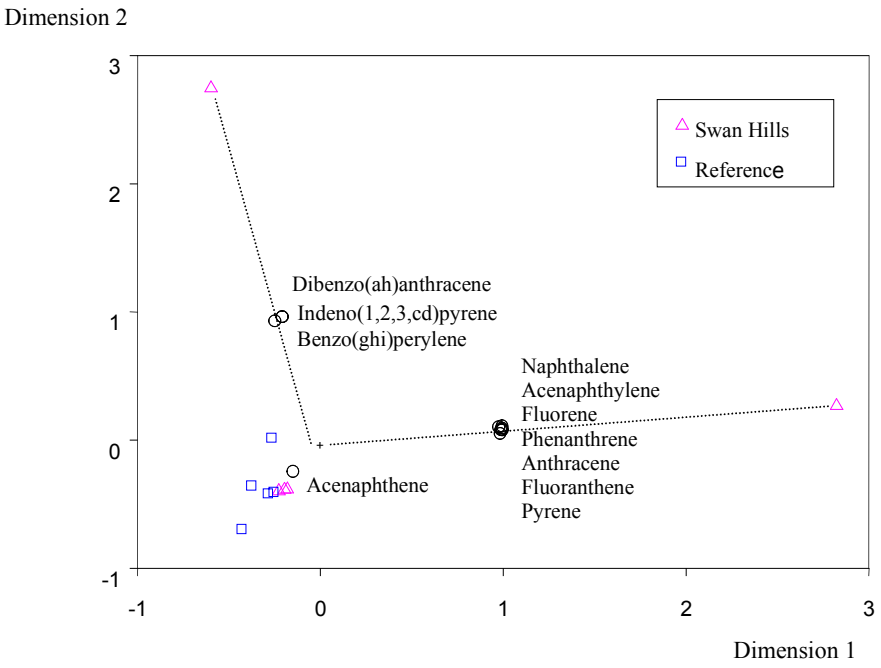

Figure 3 Distribution patterns of PAHs detected in deer liver samples from the Swan Hills and Virginia Hill area. Circles represent individual compounds as labeled beside.

Acknowledgements
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