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POLYCYCLIC AROMATIC HYDROCARBONS IN CREOSOTE IMPREGNATED WASTE MATERIALS FROM ACROSS WESTERN CANADA

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Creosote Impregnated Waste Materials (CIWMs) such as out-of-service railroad ties, telephone poles and marine pilings were assessed for toxicity in 1991 as part of the Priority Substances List under the Canadian Environmental Protection Act (CEPA). During the assessment, insufficient data was found on the polycyclic aromatic hydrocarbon (PAH) components in CIWMs, making the evaluation of potential environmental and health risks impossible. Analyses for PAHs listed on the USEPA Priority Pollutants List were carried out on out-of-service railroad ties taken from four locations across Western Canada. Each sample was extracted, partitioned, fractionated and analyzed by gas chromatography-mass spectrometry. Relatively high values of PAHs were found in approximately half of the samples. The concentration of each PAH varied from non-detected to several thousand ppm, however, the relative amounts of the various PAHs were similar in the positive samples.

KEY WORDS: Gas chromatography, mass spectrometry, creosote, wasted materials, polycyclic aromatic hydrocarbons, railroad ties.

INTRODUCTION

A Priority Substances List was developed under the Canadian Environmental Protection Act (CEPA) to identify substances and materials which might pose a threat to human health or the Canadian environment. Creosote Impregnated Waste Materials (CIWMs) were identified as one of the materials which needed further assessment to determine if regulation under CEPA was appropriate. There was some evidence to show the CIWMs still contained significant quantities of polycyclic aromatic hydrocarbons (PAHs). A method was developed for the analysis of PAHs in representative CIWMs (out-of-service railroad ties). The out-of-service railroad ties that were targeted were those that had just recently been taken out of service at four different locations across Western Canada (Surrey, Vernon, Winnipeg and Regina). The PAHs investigated were acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene.

EXPERIMENTAL

Sampling

In 1991, samples from 61 out of service railroad ties were taken. Although the history of these ties was not documented, some of the ties had a metal pin with a number which indicated the year that the tie had been put into service. If the pin markers were correct, some of the ties had been in service for at least 60 years. It was initially assumed that all ties sampled were treated with creosote.

Samples were taken from at least 15 out of service railroad ties at each location. Each sample represented one railroad tie. Representative cores were taken with a 5 mm wide increment bore from each railroad tie. The cores were removed and subsampled to obtain wood specimens ranging from the tie surface to a depth of 50 mm into the wood. Specimens from twenty cores were composited to make up a representative sample. Two ties from each location were sampled in duplicate as a check on reproducibility. Untreated wood (recently produced spruce dimensional lumber) was sampled in the same manner for both blanks and spikes.

Method

The analytical method used was adapted with modifications from work described by Rotard and Mailahm⁽¹⁾. Each sample (10 g) was air dried at room temperature and Soxhlet extracted with dichloromethane for 24 hours. This dichloromethane extract was concentrated to 30 ml and washed 3 times with 10 ml of 1 N sulfuric acid and 3 times with 10 ml of 1 N sodium hydroxide solutions, respectively. The extract was then dried by passing it through a column packed with 15 g sodium sulphate and solvent exchanged into cyclohexane. The cyclohexane extract was concentrated to approximately 2 ml and percolated through 15 g alumina with 100 ml cyclohexane and concentrated to 10 ml final extract for instrumental analysis. Analysis was carried out using a HP5970 GC/MSD in the electron impact (70 eV), selective ion monitoring mode (ions monitored listed in Table 1). For the GC, a DB-5 capillary column, 30 m long, 0.25 μ m film thickness, 0.23 mm I.D (J & W Scientific) was used with helium carrier gas at 10 psi head pressure. The splitless injector was set at 280°C with the GC temperature programmed at 80°C for 1 min, 80°C to 200°C at 15°C/min, hold at 200°C for 5 min, 200°C to 300°C at 8°C/min and hold at 300°C for 10 min. The transfer line was set at 280°C.

For quality control purposes, blanks, replicates, reagent spikes and untreated wood spikes were prepared and analyzed in the same manner. One spike and one blank were analyzed along with each set of 10 samples.

RESULTS AND DISCUSSION

The results showed that the levels of PAHs in the CIWMs varied from non-detected (detection limits listed in Table 1) to several thousand ppm from one sample to another. Approximately half of the railroad ties contained relatively high concentrations of a number of the PAHs (Table 2) Those samples with high concentration levels showed the same relative PAH concentration pattern (Figure 1), with the medium molecular weight

Table 1 GC-MS conditions.

Group	PAHs	Abbrev	SIM ions		Dwell time (ms)	Relative retention times	Detection limits ($\mu\text{g/g}$)
			Pri	Sec			
1	Acenaphthylene	AY	152	151	50	1.00	0.50
	Acenaphthene	AE	153	154	–	1.04	0.50
2	Fluorene	F	166	165	175	1.15	0.50
3	Phenanthrene	PH	178	176	175	1.45	0.50
	Anthracene	A	178	176	–	1.47	0.50
4	Fluoranthene	FL	202	101	175	2.00	0.50
	Pyrene	P	202	101	–	2.09	0.50
5	Benzo(a)anthracene	BaA	228	226	175	2.60	0.50
	Chrysene	CH	228	226	–	2.62	0.50
6	Benzo(b)fluoranthene	BbF	252	253	175	2.99	1.25
	Benzo(k)fluoranthene	BkF	252	253	–	3.00	1.25
7	Benzo(a)pyrene	BaP	252	253	–	3.11	1.25
	Indeno(1,2,3-c,d)pyrene	IP	276	277	80	3.6	2.5
	Dibenzo(a,h)anthracene	DBahA	278	279	–	23.61	2.50
	Benzo(g,h,i)perylene	BghiP	276	277	–	3.73	2.50

Table 2 CIWM analysis results summary.

Analyte	Avg of 27 Conc. samples ($\mu\text{g/g}$)	Conc. range of the 27 samples ($\mu\text{g/g}$)
AY	11.0	ND – 42.0
AE	1410	139 – 5600
F	1420	178 – 4910
PH	3720	654 – 13500
A	1170	273 – 5300
FL	2560	481 – 7820
P	1670	356 – 5110
BaA	599	167 – 2110
CH	681	220 – 2260
BbF	421	82.0 – 948
BkF	310	52.0 – 811
BaP	342	86.0 – 656
IP	193	18.0 – 389
DBahA	64.0	ND – 187
BghiP	142	28.0 – 339

PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene) being the most abundant, while acenaphthylene and the higher molecular weight PAHs being less abundant or not even appearing in a number of the samples. Comparison of out of service ties with recently creosote treated wood showed a loss of the lighter PAHs especially acenaphthene, fluorene and phenanthrene in the out of service tie.

Many of the less concentrated samples did not contain detectable levels of any of the target analytes. Whether these had been sampled from ties that had not been treated with creosote was difficult to determine. Some of the samples contained very high levels of pentachlorophenol, indicating that some ties had been treated with either pentachlorophenol only or a combination of pentachlorophenol and creosote.

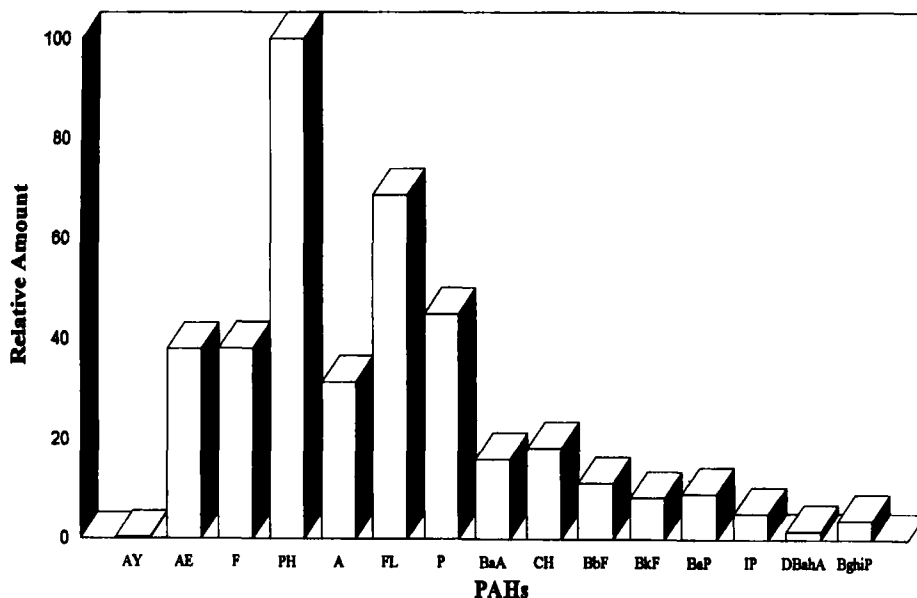


Figure 1 PAHs Profile in Out-of-Service Ties.

Table 3 Untreated wood spikes.

Analyte	Amount ($\mu\text{g/g}$)	Avg. % Rec. of 7 spikes	%RSD
AY	20.0	103.6	9.6
AE	20.0	101.8	9.1
F	20.0	106.9	6.8
PH	20.0	112.5	7.2
A	20.0	109.3	6.7
FL	20.1	117.4	11
P	20.0	110.4	9.4
BaA	20.0	118.2	12
CH	20.0	112.0	11
BbF	20.0	107.2	11
BkF	20.0	108.0	13
BaP	20.0	106.8	14
IP	20.0	110.1	17
DBahA	20.0	109.1	20
BghiP	20.0	104.2	16

For most analytes, spike percent recovery ranged between 100 and 120% and precision (%RSD) was below 15% (Table 3). The replicate samples showed that precision was good for all analytes (Table 4). No measurable amount of analytes were detected in the blanks.

Table 4 Replicate analysis.

<i>Analyte</i>	<i>Average Conc.</i> <i>($\mu\text{g/g}$)</i>	<i>%RSD</i>
AY	6.40	4.6
AE	376	2.2
F	358	3.9
PH	857	1.7
A	158	4.7
FL	691	0.6
P	426	1.6
BaA	91.8	6.6
CH	108	5.4
BbF	18.3	0.7
BkF	13.5	16
BaP	13.8	6.3
IP	3.70	4.8
DBahA	1.10	17
BghiP	3.40	7.6

CONCLUSION

Results indicated that out-of-service railroad ties (CIWMs) can contain very high concentrations of PAHs even after several decades of use. Present practice allows the reuse and unregulated disposal of railroad ties and other types of CIWMs. Further investigations are required to address the question of whether or not a hazard is being posed to health and the environment from the disposal or reuse of CIWMs.

References

1. W. Rotard and W. Mailahm, *Anal. Chem.*, **59**, 65-69, (1987).