POLYCYCLIC AROMATIC HYDROCARBONS, PENTACHLOROPHENOL, DIOXINS AND FURANS IN WASTE WOODEN SLEEPERS ON THE RECYCLING MARKET

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Introduction

Various chemicals are used in wood preservation and protection. Creosote, a wood preservative used worldwide for centuries, consists mainly of polycyclic aromatic hydrocarbons (PAHs), including possible carcinogens and teratogens such as benzo[a]pyrene (B[a]P).[1-3] Some practices of applying creosote to wood include the use of chlorophenols (CPs) in combination.[3-5] These practices create the potential for exposing humans or the environment to CPs and their impurities, dibenzo-p-dioxins and dibenzofurans (PCDD/DFs), as well as to the PAHs in wood products treated with creosote.

In Japan, the main use of wood treated with creosote is for wooden railway sleepers (railroad ties). The amount of pressure-treated sleepers produced decreased during the 1990s, but in recent years it has stabilized around 30 000 m^3 a year. This means that a comparable amount of used sleepers has been and will continue to be released each year. Some used sleepers appear at gardening and do-it-yourself shops as materials for outdoor construction, garden furniture, and interior ornament.[6] PAHs, CPs, and PCDD/DFs remain in these sleepers, posing a risk of exposure to humans when the sleepers are cut, installed inside buildings, placed in contact with foodstuff, or placed in playgrounds, gardens, or other sites where skin contact is possible.

The objectives of this study were to determine the chemical characteristics of used sleepers as a contribution to risk analysis and risk management in their recycling. Creosote, used sleepers, and other wood were bought from shops and analyzed for PAHs, pentachlorophenol, and PCDD/DFs.

		Origin	Coments
		DIY shop	-canned for DIY
Sleeper A	cross-section	DIY shop	-no information about service life (same for other sleepers)
	interior	DIY shop	-inside of sleeper A
	surface	DIY shop	-surface of sleeper A
Sleeper B	surface	gardening shop	-used wooden railway sleeper B
Sleeper C	surface	gardening shop	-used wooden railway sleeper C
		DIY shop	-scrap for children's handicrafts and toys
		convenience store	-chopsticks

Materials and Methods

Samples, summarized in Table 1, were bought from a do-it-yourself (DIY) shop and a gardening shop in Japan. Wood subsamples were collected by sawing several grams of materials.

	Creosote				
		interior	surface	A	B
Naphthalene	56,000,000	5,400	8,100	3,700	110	3,000
Acenaphthylene	950,000	N.D.	19	360	23	47
Acenaphthene	64,000,000	1,200	5,600	1,300	93	190
Fluorene	21,000,000	11,000	16,000	16,000	690	290
Phenanthrene	56,000,000	85,000	110,000	77,000	1,700	1,200
Anthracene	17,000,000	15,000	24,000	36,000	610	75
Fluoranthene	10,000,000	6,300	7,200	11,000	51	83
Pyrene	9,000,000	63,000	66,000	77,000	360	79
Benz[a]anthracene	2,500,000	38,000	37,000	55,000	7	67
Chrysene	2,800,000	120,000	130,000	130,000	30	260
Benzo[b]fluoranthene	900,000	9,600	15,000	15,000	N.D.	420
Benzo[k]fluoranthene	950,000	1,800	3,400	3,800	N.D.	190
Benzo[a]pyrene	930,000	26,000	25,000	55,000	N.D.	280
Indeno[1,2,3-cd]pyrene	590,000	1,200	1,100	420	N.D.	56
Benzo[g,h,i]perylene	250,000	11,000	11,000	14,000	1	32
Dibenz[a,h]anthracene	110,000	11,000	11,000	15,000	N.D.	6
Total	240,000,000	410,000	470,000	510,000	3,700	6,300

				Sleeper B	Sleeper C	Untreated	Creosote
		interior	surface	surface	surface	wood A	
	-	250,000	280,000	640	290	-	-
2378-T4CDD	0.0091	N.D.	(0.0068)	N.D.	N.D.	N.D.	N.D.
T4CDDs	0.14	0.023	0.055	0.23	N.D.	0.026	N.D.
12378-P5CDD	0.39	0.012	0.25	N.D.	N.D.	N.D.	N.D.
P5CDDs	2.6	0.39	0.84	0.12	N.D.	N.D.	N.D.
123478-H6CDD	2.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
123678-H6CDD	56	66	120	N.D.	N.D.	N.D.	N.D.
123789-H6CDD	3.3	2.2	4.0	N.D.	N.D.	N.D.	N.D.
H6CDDs	170	150	260	0.24	N.D.	N.D.	N.D.
1234678-H7CDD	1,300	1,000	1,400	0.24	(0.013)	0.017	0.051
H7CDDs	1,900	1,600	2,100	0.75	0.026	0.03	0.051
O8CDD	4,400	1,900	1,800	1.2	0.063	0.082	0.21
	6,500	3,700	4,200	2.5	0.089	0.14	0.26
TEQ*	20	18	27	0.0025	0.0000063	0.00018	0.00053
2378-T4CDF	0.5	0.71	1.4	0.033	N.D.	N.D.	0.028
T4CDFs	9.1	3.8	27	0.58	N.D.	0.0034	0.53
12378-P5CDF	2.6	3.8	7.0	0.026	N.D.	N.D.	N.D.
23478-P5CDF	3.4	2.6	4.8	0.022	N.D.	N.D.	N.D.
P5CDFs	290	76	140	0.34	N.D.	0.0054	N.D.
123478-H6CDF	8.8	9.8	18	0.028	N.D.	N.D.	N.D.
123678-H6CDF	5.7	8.8	7.3	0.026	N.D.	N.D.	N.D.
123789-H6CDF	N.D.	1.7	3.3	N.D.	N.D.	N.D.	N.D.
234678-H6CDF	3.5	4.7	9.6	0.055	N.D.	N.D.	N.D.
H6CDFs	290	450	860	0.35	N.D.	N.D.	N.D.
1234678-H7CDF	90	75	130	0.12	(0.0084)	N.D.	N.D.
1234789-H7CDF	6.8	4.1	8.4	0.030	N.D.	N.D.	N.D.
H7CDFs	400	290	520	0.26	0.0084	N.D.	N.D.
O8CDF	290	110	200	0.15	N.D.	N.D.	N.D.
	1,300	930	1700	1.7	0.0084	0.0088	0.53
TEQ*	4.7	4.9	8.1	0.028	0	0	0.0028
total PCDDs+PCDFs	7800	4600	5900	4.2	0.097	0.15	0.79
	24	22	35	0.030	0.0000063	0.00018	0.0034

* : WHO-1998-TEF - : not measured N.D.: under the detection limit of actual measurement

Wood samples were Soxhlet extracted with toluene for 16h. Creosote sample was liquid-liquid extracted three times with dichloromethane.

The Japanese Industrial Standard (JIS) method K 0312 was adapted for analysis of PCDD/DFs. For analysis of PAHs (16 PAHs defined as priority pollutants by US EPA), extracts were added d-labeled internal standards and concentrated. Extracts were cleaned up by DMSO partition method,[7] and concentrated. Then the samples were chromatographed on a silica gel column, and eluted with 50% (v/v) dichloromethane-hexane. For analysis of PCP, extracts were added internal standards and

concentrated. Then the samples were chromatographed on a silica gel column, and eluted with 50% (v/v) dichloromethane-hexane.

Chemicals were identified and quantitated by high-resolution capillary column gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS).

Results and Discussion

PAHs

Concentrations of PAHs in creosote, sleeper A and untreated woods are shown in Table 2. All 16 PAHs was found in creosote at a total concentration of 240 000 ppm, corresponding to 24% of product. The amount of B[a]P in creosote was 930 ppm. This exceeds the European limit of 500 ppm, above which the sale and use of creosote and its products in Europe are banned.

The concentration of PAHs in sleeper A was approximately 2 orders of magnitude higher than that in the untreated woods. The profile of individual PAHs in sleeper A was different from that in creosote: 2- and 3- ring PAHs predominated in creosote, but 4- and 5- ring PAHs predominated in sleeper A. This result suggests that low-molecular-weight PAHs may be emitted from sleepers just after production and during their service life by leaching, volatilization, and perspiration,[1,4] but that high-molecular-weight PAHs tend to remain.

PCP, PCDDs, PCDFs

Concentrations of PCP, PCDDs, and PCDFs in samples are shown in Table 3. The concentrations in sleeper A were approximately 4 orders of magnitude greater than those in the untreated wood and creosote. Figure 1 shows the profiles of PCDD/DF congeners in sleeper A. The prominence of highly-chlorinated dioxins suggests that the residual PCDD/DFs were impurities of PCP.

There was no difference in PCP, PCDD, or PCDFs levels between the interior and surface of sleeper A. This result suggests that good saturation was achieved during PCP application.

On the other hand, concentrations in sleepers B and C were 3 to 5 orders of magnitude lower than those in sleeper A. In particular, the PCDD/DFs concentrations in sleeper C were less than those in the untreated wood, indicating that the sleeper was untreated.

Application of PCP with creosote

Sleeper A contained relatively high concentrations of PCP and PCDD/DFs, and so it seems to have been treated with PCP in addition to creosote. Figure 2 shows 4 times at which it could have been added.[3-5,8]

Fries et al.[9] collected wood samples from livestock facilities, analyzed them for PCP and PCDD/DFs, and classified the results by the relationship between the chemical concentrations and the methods of PCP application (summarized in Table 4), according to a US Department of Agriculture standard. This classification indicates that sleeper A was treated by surface application according to PCP level, and by pressure treatment and surface application according to PCDD/DF levels. Although we do not know the amount and time of application for sleeper A, the relatively high concentration in the heart of the wood and the higher concentration of PCP than of PCDD/DFs indicate the possibility of pressure treatment with creosote in combination with PCP.

The concentration of PCP in sleeper B was low, but the levels of PCDD/DFs were relatively high, and their congener profile (Figure 1) is similar to that of impurities in PCP, which suggests a low-level PCP application according to the classification by Fries et al., followed by PCP emission. As well, waste wood treated with copper chrome arsenate or low-level creosote (Table 4),[10] contained the same levels of PCDD/DFs. It seems that PCP had been used widely for low-level application in sawmills to prevent fungus growth in undried lumber, [4,8] and that this level can be detected whether or not PCP is applied with other chemicals. Sleeper C seems to have been untreated.

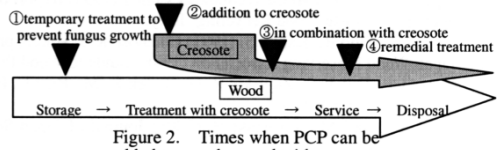

Figure 2. Times when PCP can be added to wood treated with creosote

Source	Classification	PCP (μg/g	PCDD/DFs (ng-TEQ/g)	to wood
from livestock facilities in the USA	PCP < LQ	< Limit of quantitation	0.011-1.7	untreated with PCP
	PCP low	2.5 82	0.016-2.4	low-level application
	PCP intermediate	110 880	1.6-53	surface application
	PCP high	1,600 8,500	27-310	pressure treatment
in Japan (Sakai et al., 1999)	CCA-treated waste wood	3.1 (total CPs: 5.4)	0.0068	low-level application
	Creosote-treated waste wood	0.088 (total CPs: 8.5)	0.018-0.029	low-level application with CPs
	Untreated waste wood	0.17 (total CPs: 0.69)	0.0023-0.0074	untreated with PCP
Wooden produts tested in this study	Sleeper A (cross-section)	-	24	pressure treatment or surface application
	Sleeper A (interior)	250	22	
	Sleeper A (surface)	280	35	
	Sleeper B (surface)	0.64	0.03	low-level application
	Sleeper C (surface)	0.29	0.0000063	untreated with PCP
	Untreated wood A	-	0.00018	untreated with PCP

Not all wooden sleepers contain PCP, but some contain 10 ppb-TEQ levels of PCDD/DFs, which are impurities of PCP, and are freely available on the market. Further research about the origins of such sleepers or other waste wood is desirable. Risk assessment and risk control also need to be examined.

Acknowledgements

The authors are grateful for financially support of this study by a Waste Management Research Grant of the Environment Ministry, 2001, for “Studies on chemical cycles and their control”, a research project organized by the Japan Waste Research Foundation.

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