

21
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A REVIEW OF OCCURRENCES AND TREATMENT OF POLYNUCLEAR
AROMATIC HYDROCARBONS

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ABSTRACT

A literature review has been conducted into the scope of PAH contamination of raw, finished, and distributed waters. The concentrations of PAHs in drinking water sources range from nanogram to microgram-per-liter quantities. Conventional treatment (flocculation, sedimentation, chlorination, and filtration) appears to substantially reduce total PAH concentrations present at higher concentrations in source waters. A major factor in this reduction is the removal of PAHs adsorbed onto particulate matter. The role of chlorination is not clear and reactions of PAHs with chlorine may in fact produce products which themselves are deleterious. Activated carbon can further assist in PAH removal. However, it may be inappropriate for treatment of PAHs present at low concentrations. Water entering the distribution system can become recontaminated via contact with reservoirs and pipes coated with coal-tar or asphalt based products.

Introduction

Polynuclear aromatic hydrocarbons (PAHs) are compounds of two or more aromatic rings, where adjacent rings share two carbon atoms. The molecular weights and relative carcinogenic potential of some PAHs that have been detected in water are given in Table I. The high molecular weight and nonpolar nature of PAHs afford compounds of low solubility in water. The solubility ranges from 1.6 mg/l for phenanthrene (Ph) to 0.01 - 4 µg/l for benzo(a)pyrene (B(a)P) (Davis et al, 1942; Andelman and Snodgrass, 1974). The concentrations of PAHs in surface waters, however, are in part dependent on the organic loading of the aqueous system, which affects PAH solubilities, and on the amount of suspended particulate matter to which PAHs can adsorb. This is exemplified by the occurrence of up to 1000 µg/l of B(a)P in coke or oil-gas plant effluents (Wedgewood and Cooper, 1956). For raw water sources, the concentrations are typically much lower.

Scope of PAH Contamination

Among the first studies performed to determine the magnitude of PAH concentrations in water were those of Borneff. These investigations dealt primarily with surface and ground waters located in Germany. The data from one such study (Borneff and Kunte, 1964) are listed in Table II. (Data given in these and subsequent tables and in the text are as reported in the cited references. No attempt was made to evaluate sampling and analytical procedures used or the significant figures reported.) Surface waters in the Soviet Union have been shown to be vulnerable to PAH contamination as well (Table III) (Andelman and

Table I
PAHs Found in Water^a

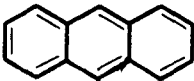
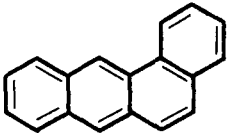
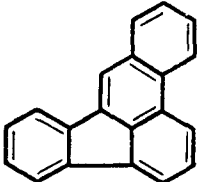
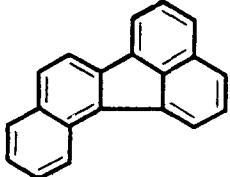
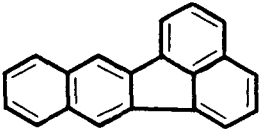
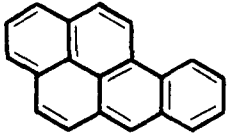
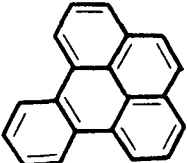
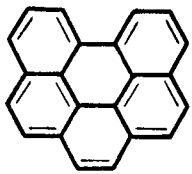
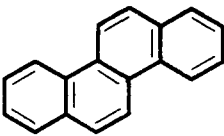
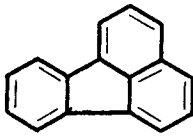
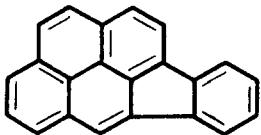
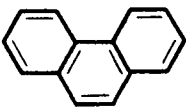
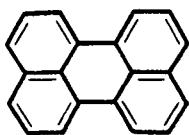
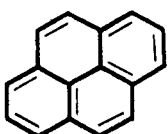
Structure	Name	Molecular Weight	Relative Carcinogenic Activity ^b
	Anthracene An	178	-
	Benzo(a)anthracene B(a)A	228	+
	Benzo(b)fluoranthene B(b)F	252	++
	Benzo(j)fluoranthene B(j)F	252	++
	Benzo(k)fluoranthene B(k)F	252	-
	Benzo(a)pyrene B(a)P	252	+++ ^c
	Benzo(e)pyrene B(e)P	252	-

Table I
PAHs Found in Water^a

Structure	Name	Molecular Weight	Relative Carcinogenic Activity ^b
	Benzo(ghi)perylene B(ghi)P	276	-
	Chrysene Ch	228	<u>±</u>
	Fluoranthene Fl	202	-
	Indeno(1,2,3-cd)pyrene IP	276	+
	Phenanthrene Ph	178	-
	Perylene Per	252	-
	Pyrene Pyr	202	-

a Sorrell, et.al., 1977.

b +++, ++, strongly carcinogenic; +, carcinogenic; ±, uncertain or weakly carcinogenic; -, not carcinogenic (NAS, 1972).

c Discussed in NAS Report (1977).

Table II
Concentrations (ng/l) of PAHs in Surface and Ground Waters in Germany^a

Location	Fl	Pyr	B(a)A	B(j)F	B(b)F	Ch	B(a)P	B(ghi)P	B(k)F	IP
Groundwater I May, 1963	42.0	b	b	b	0.8	b	0.1	0.8	0.8	0.4
Groundwater II August, 1963	26.2	b	1.0	1.0	1.0	b	0.6	0.5	0.5	0.5
Groundwater III January, 1964	169.0	104.0	23.2	10.0	11.5	b	23.4	17.5	10.0	12.6
Danube R. at Ulm April, 1964	94.0	74.5	11.0	10.1	24.2	b	0.6	9.5	7.7	9.5
Bodensee May, 1964	21.4	b	5.0	13.0	7.7	b	1.3	3.2	2.7	2.6
Danube R. at Ulm May, 1964	61.0	0.3	14.0	23.4	23.9	b	b	9.5	14.1	16.4
Main R. at Seligenstradt July, 1963	128.3	109.8	14.4	35.7	32.1	38.2	2.4	21.2	10.6	32.0
Main R. at Seligenstradt April, 1964	192.0	92.8	16.2	75.5	67.0	b	6.5	25.9	21.6	23.7
Rhine R. at Mainz May, 1964	146.0	b	53.5	21.3	77.8	b	49.2	43.2	27.4	35.8
Rhine R. at Mainz March, 1964	258.0	2.0	185.0	150.0	156.0	b	114.0	134.0	117.0	123.0
a Borneff and Kunte, 1964. b Not reported.										

Table III

Occurrences of Benzo(a)pyrene in Surface Waters in the Soviet Union^a

Source	Concentration, ng/l
Moscow Reservoirs	4,000 - 13,000
Volga River (below refinery)	0.1
Pskov Region	<0.1
Sunzha River (3-4 km below refinery)	50 - 3,500
Sunzha River (25 km below refinery)	70 - 1,060

a Andelman and Snodgrass, 1974.

Snodgrass, 1974). Their ubiquity is further illustrated by the data in Tables IV (Acheson et al, 1976) and V (Lewis, 1975) where both the Thames and Severn Rivers in England were investigated. These data indicated that individual PAHs can occur in concentrations ranging from the low ng/l to $\mu\text{g/l}$ levels. The studies of waters in Europe are currently being complemented by analyses of waters within the United States. The U.S. EPA has been responsible for the bulk of data collected, which to date have indicated that U.S. waters also contain PAHs.

The first attempt to gain comprehensive data on PAH levels in U.S. waters was the National Organic Monitoring Survey, Phase I and II, (NOMS, 1978), where mostly finished waters were sampled and analyzed. These data indicated the presence of fluoranthene in several supplies with an observed maximum value of 80 ng/l. The analyses of raw and/or finished waters of 11 supplies in the U.S. are reported in another study recently completed (Saxena et al, 1977; Basu et al, 1978) (Table VI). A varying amount of PAH contamination in raw waters, 4.7 - 1600 ng/l for 6 PAHs was found. This variation is believed to be a function of industrial contamination. In general, the finished water data show reduced concentration of PAHs. Note that some of the supplies use activated carbon in the treatment process. The PAH reduction in raw water through conventional treatment is apparent from data gathered by the Technical Support Division, ODW, US EPA, (Table VII). However, reduction by treatment is not demonstrated in every case. For example, while data from Cincinnati, OH, Cape Girardeau, MO, Wheeling, WV, and Jefferson Parish, LA show excellent removal of 7 PAHs (chrysene through indeno(1,2,3-cd)pyrene) using conventional treatment,

Table IV
PAH Concentrations (ng/l) in the Thames River^a

Compound	Location		
	Kew Bridge	Albert Bridge	Tower Bridge
Fluoranthene	180	20	180
Pyrene	260	50	230
Benzo(a)anthracene and Chrysene	140	270	530
Benzo(b)fluoranthene ^b			
Benzo(j)fluoranthene	240	150	430
Benzo(k)fluoranthene			
Benzo(a)pyrene ^b			
Benzo(e)pyrene	210	c	130
Perylene	40	c	120
Indeno(1,2,3-cd)pyrene	100	70	110
Benzo(ghi)perylene	40	40	30

a Acheson, et.al., 1976.
 b Summation of isomers.
 c Not reported.

Table V
PAH Concentrations (ng/l) in the Severn River^a

Compound	Atcham	Bewdly	Location		
			Holt Fleet	Haw Bridge	Maisemore
Fluoranthene	15	28.5	21.5	25.2	128.4
Benzo(a)pyrene	1.5	6.5	9.2	13.5	12.5
Indeno(1,2,3-cd)pyrene	6.1	3.9	7.8	10.0	7.9
Benzo(k)fluoranthene	0.8	4.0	3.1	7.7	3.4
Benzo(ghi)perylene	2.0	6.3	10.5	11.3	7.6

a Lewis, 1975.

Table VI

Concentrations (ng/l) of PAHs in Raw and Finished Waters in the United States^a

City	Fluoranthene	Benzo(j)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Benzo(ghi)perylene
Syracuse, NY Finished	b	b	0.4	0.3	b	0.4
Buffalo, NY Raw	b	b	0.6	0.3	b	3.8
Finished	b	b	b	0.2	b	0.7
Pittsburgh, PA ^c Raw	408.3	35.7	19.1	42.1	60.4	34.4
Finished	b	0.3	0.2	0.4	1.2	0.7
Huntington, WVA ^d Raw	23.5	5.0	3.6	5.6	9.5	10.7
Finished	2.4	0.3	0.2	0.5	1.2	2.5
Philadelphia, PA Raw	114.3	42.6	33.0	41.1	72.4	48.4
Finished	8.9	b	b	0.3	1.7	4.0
Endicott, NY Finished	4.3	0.2	b	0.2	0.7	2.9
Hammondsport, NY Finished	b	0.3	0.1	0.3	0.9	1.9
New York City, NY Finished	b	1.2	0.7	0.5	2.2	1.8
Lake George, NY Finished	b	0.3	0.1	0.3	0.9	2.6
New Orleans, LA Finished	b	b	0.6	1.6	b	2.2
Wheeling, WVA ^e Raw	756.5	180.7	115.5	206.4	180.0	147.0
Finished	94.5	1.4	b	2.1	7.8	32.7
<p>a Saxena, et.al., 1977. b Indicates not detected, with a detection limit ranging from 0.1 - 4.6 ng/l. c Two stage activated carbon treatment; powdered A.C., then granulated A.C. filtration. d Granulated A.C. filtration. e Addition of powdered A.C.</p>						

Table VII
PAHs in Raw and Finished Waters in the United States^a (ng/l)

Compound	Cincinnati OH		New Orleans LA Distributed	Miami FL		Seattle WA		Portland OR Raw	Columbus OH		Cape Girardeau MO		Wheeling WV		Jefferson Parish LA		Tucson AZ Raw
	Raw	Fin		Raw	Fin	Raw	Fin		Raw	Fin	Raw	Fin	Raw	Fin	Raw	Fin	
Ph	14	10	14	6	14	10	12	8	3	14	5	9	4	20	14	10	
Fl	<7	<3	<5	<4	<4	<4	<8	4	1	11	1	15	4	25	7	<2	
Pyr	<14	<4	<3	<4	<6	<4	<6	6	<1	9	<1	15	2	18	3	<2	
1-MP	<6	<4	b	<2	<1	<1	<1	<1	<1	<1	<1	5	<1	5	<2	<2	
An	b	b	b	b	b	b	b	b	b	1	<1	b	<1	2	<2	<2	
Ch	4	<1	<1	<1	2	<1	2	<1	<1	5	<1	8	<1	8	<2	<2	
B(a)A	4	<1	<1	<1	<1	<1	<1	<1	<1	4	<1	9	<1	9	<2	<2	
Per	b	<1	<1	<1	<1	<1	<1	<1	<1	b	<1	<4	<1	7	b	b	
B(e)P	b	<1	<1	<1	<1	<1	<1	<1	<1	b	<1	b	<1	<14	<2	<2	
B(a)P	9	<1	<1	<1	<1	<1	<1	<1	<1	4	<1	13	<1	12	<2	<2	
B(ghi)P	<1	<1	<1	<1	<1	<1	<1	<1	<1	4	<1	9	<1	7	b	b	
B(b)F	5	<1	<1	<1	<1	<1	<1	<1	<1	4	<1	16	<1	9	<2	<2	
B(k)F	3	<1	<1	<1	<1	<1	<1	<1	<1	2	<1	7	<1	3	<2	<2	
DiB(ah)A	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<2	<2	<2	
IP	<4	<1	<1	<1	<1	<1	<1	<1	<1	<3	<1	<12	<1	<9	<2	<2	
Total	39	10	14	6	16	10	14	18	4	58	6	107	10	125	24	10	
<p>a Sorrell, et.al., 1979. b Not analyzed.</p>																	

data from Miami and Seattle indicated no removal for the lower molecular weight (PAHs) phenanthrene, fluoranthene, and pyrene.

Removal of PAHs From Contaminated Waters

Effective removal of PAHs from raw water appears to be closely related to particulate removal and thus, conventional water treatment practices are generally quite effective. Data in Table VIII (Lewis, 1975) indicates consistently higher quantities of PAHs associated with the suspended solids, than with the aqueous portion. In their study of the treatment process, Crane et al. (1978) found clarification, i.e. removal of particulates, reduced the PAH level from 50 ng/l to less than 10 ng/l (Figure 1). It also can be seen that chlorination and the use of activated carbon (most probably powdered) can affect PAH reduction. Samples from the point of prechlorination and addition of activated carbon reveal a PAH reduction of 35 ng/l. What portion of this reduction is due to activated carbon is not clear, as the chlorination process itself can contribute to PAH reduction.

Chlorination

The effects of chlorination on PAHs have been investigated by several researchers. Il'nitskii et al (1971) found a PAH reduction after 30 min contact time with 0.5 mg/l chlorine residual. A summary of some of the investigations concerning the reactions of PAHs in the presence of chlorine, is given in Table IX (Oyler and Carlson, 1978). The removal of PAHs that might be attributable to chlorination during normal treatment is given in Table X (Harrison et al., 1976). These data were obtained after an initial chlorine dose of 5 mg/l at a pH of 7.5; the free chlorine residual at 3 hours contact time was 0.5 mg/l.

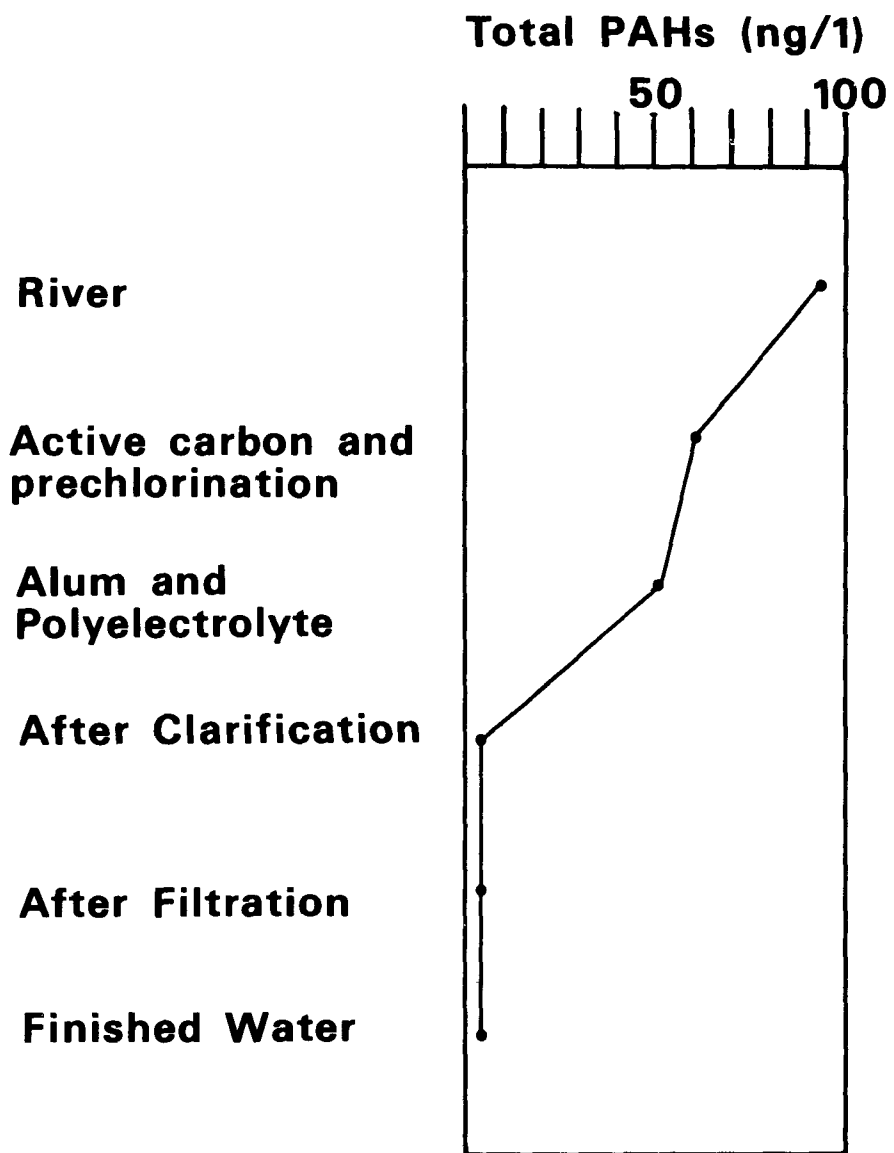


FIGURE 1

Table VIII
Concentrations (ng/l) of PAHs in the River Trent and its Tributaries^a

Location	PAHs in Suspended Solids ^b					PAHs in Solution ^c					
	F1	B(a)P	IP	B(k)F	B(ghi)P	F1	B(a)P	IP	B(k)F	B(ghi)P	
R. Trent - Hanford	165.0	57.0	39.0	33.0	72.0	15.0	0.5	1.2	0.5	1.6	
R. Dove - Mapleton	18.0	8.8	5.8	6.8	12.5	4.0	0.2	0.8	0.2	0.9	
R. Dove - Above Rocester	12.0	7.8	4.5	4.7	10.5	4.8	0.2	0.4	0.2	0.7	
R. Trent - Yoxall	121.1	51.0	46.0	33.0	65.0	4.8	0.4	0.6	0.3	1.0	
R. Trent - Walton	150.0	95.0	66.0	76.0	138.0	6.6	0.9	0.7	0.9	1.9	
R. Amber - Ambergate	20.0	15.0	24.0	11.0	57.0	16.0	1.8	8.0	1.0	11.0	
R. Trent - Willington	77.0	54.0	42.0	36.0	71.0	6.0	0.4	0.4	0.5	1.1	
R. Derwent - Little Eaton	22.0	9.4	6.1	8.4	13.6	3.7	0.2	0.0	0.2	0.8	
Reservoir Water - Derwent	1.2	0.8	0.6	0.5	1.7	1.3	0.1	0.7	0.1	0.4	
Final Treated Water - Derwent		No Suspended Matter					0.8	0.1	0.0	0.1	0.4
R. Soar - Kegworth	14.0	14.0	11.0	13.0	26.0	1.1	0.1	0.2	0.3	0.7	
R. Trent - Keadby	928.0	504.0	195.0	265.0	688.0	15.0	0.2	0.2	0.1	0.5	

a Lewis, 1975.
b The particulate matter filtered from water sample.
c Filtrate of water sample.

Table IX

Aqueous Chlorination Reactions of Polynuclear Aromatic Hydrocarbons: Selected Results From Literature Reports^a

Compound	Compound ug/l	Chlorine mg/l	pH	Time (Hr)	Products/Comments	Reference
benzo(a)pyrene	1	0.5		0.5	81% reduction 94% reduction	Tralsttman and Manita, 1966
	1	0.3		0.5 2	82% reduction 92% reduction Products identified: 5-chloro-3,4-benzo- pyrene and 3,4-benzo- pyrene quinone	
benzo(a)pyrene	5	0.3		3	50% reduction	Graef and Nothhafft, 1963
				3	50% reduction	
	2	0.5	22	83% reduction		
benzo(a)pyrene	4	0.4- 0.6		2	50% reduction	Gabovich, et.al., 1969
				13	100% reduction	
				0.5	68-75% reduction	
				2.0	80-83% reduction	
benzo(a)pyrene	4	0.4- 0.6		24	88-90% reduction	Mueller and Reichert, 1969
				2.0	90% reduction	
				24	95% reduction	
				24	Products identified: 5-chloro-and 5, 8, 10- trichloro-derivatives	

Table IX (Cont'd)

Aqueous Chlorination Reactions of Polynuclear Aromatic Hydrocarbons: Selected Results From Literature Reports^a

Compound	Compound ug/l	Chlorine mg/l	pH	Time (Hr)	Products/Comments	Reference
benzo(a)pyrene	10.5	6		1.5	anionic detergent present 86% reduction	Sforzolini, et.al., 1971
	4.3	6		3.0	anionic detergent present 82% reduction	
	11.25	6		6.0	anionic detergent present 92% reduction	
	13.62	6		1.5	Tween 80 present ^b 85% reduction	
	12.70	6		3.0	Tween 80 present 88% reduction	
	13.50	6		6.0	Tween 80 present 92% reduction	
aromatic fraction fraction of diesel fuel		100	7.2	1	chloro-C ₂₋₃ naphthalene identified	Reinhard, et.al., 1976
				30	100% reduction of naphthalene, phenathrenes, anthracenes	
naphthalene	10000	30	6.0	16	66% naphthalene, 3-2% 1-chloronaphthalene, and 1% 1,4-dichloronaphthalene	Smith, et.al., 1977
1-methyl-naphthalene	0.53	24	4.1	3	1-chloro-4-methyl-naphthalene (73% yield)	Oyler, et.al., 1978
fluorene	0.33	1.2	7.0	0.5	fluorene (73% yield)	
anthracene	0.97	12.4	6.5	3.75	anthraquinone (78% yield)	

Table IX (Cont'd)

Aqueous Chlorination Reactions of Polynuclear Aromatic Hydrocarbons: Selected Results From Literature Reports^a

Compound	Compound ug/l	Chlorine mg/l	pH	Time (Hr)	Products/Comments	Reference
phenanthrene	0.24	3.7	6.8	0.5	phenanthrene (77% yield)	ibid
	0.23	26.3	6.0	3	phenanthrene (86% yield) 9-chlorophenanthrene (4% yield)	
	0.24	19.5	4.2	3	phenanthrene (9% yield) 9-chlorophenanthrene (38% yield)	
1-methylphenanthrene	0.18	25.6	4.0	3	monochloro-1-methylphenanthrene (8% yield)	
fluoranthene	0.24	22.0	5.9	3	fluoranthene (63% yield)	
	0.24	23.9	4.0	3	fluoranthene (42% yield) fluoranthene chlorohydrin (32% yield)	
benz(a)anthracene	30.62	6		6.0	Tween 80 present ^b 31% reduction	Sforzolini, et.al., 1977
benz(e)acephenanthrylene	43.09	6		6.0	Tween 80 present 11% reduction	
benz(k)fluoranthene	14.3	6		6.0	Tween 80 present 27% reduction	
pyrene	3.2	6		6.0	Tween 80 present 22% reduction	
pyrene	3.2	2±0.25		0.5	37% reduction distilled water	Sforzolini, et.al., 1973
benz(a)anthracene	3.05	2±0.25		0.5	83% reduction distilled water	and 1974

Table IX (Cont'd)

Aqueous Chlorination Reactions of Polynuclear Aromatic
Hydrocarbons: Selected Results From Literature Reports^a

Compound	Compound ug/l	Chlorine mg/l	pH	Time (Hr)	Products/Comments	Reference
benz(a)pyrene	3.06	2+0.25		0.5	100% reduction distilled water	
benzo(k)fluoranthene	3.08	2+0.25		0.5	23% reduction distilled water	
benz(e)acephenanthry- lene	3.04	2+0.25		0.5	15% reduction distilled water	
fluorene	200	9.8	7.0	24	65% reduction no chloro products identified	Spath, 1972
naphthalene	100	10	7.0	24	82% reduction no chloro products identified	
acenaphthalene	200	10	7.0	24	100% reduction menochloro product identified	
pyrene	50	10	7.0	24	100% reduction no chloro products identified	

a Oyler and Carlson, 1978.

b Tween 80 is a general-purpose emulsifier and surface active agent.

Table X
Concentrations (ng/l) of PAHs at Various Stages of Water Treatment Works^a

Compound	River Intake	After Reservoir	After Filtration	After Chlorination
Fluoranthene	150	140	81	45
Pyrene	100	75	45	18
Benzo(a)anthracene and Chrysene	90	72	33	12
Benzo(b)fluoranthene ^b				
Benzo(j)fluoranthene	147	132	39	21
Benzo(k)fluoranthene				
Benzo(a)pyrene ^b				
Benzo(e)pyrene	c	51	30	9
Perylene	c	39	24	c
Indeno(1,2,3-cd)pyrene	69	66	27	9
Benzo(ghi)perylene	72	63	33	9

a Harrison, et.al., 1976.
b Summation of isomers.
c Not reported.

The loss of PAHs from the filtered water averaged approximately 60%. Factors such as pH, temperature, contact time, and concentration of the chlorinating agent can have a profound effect on removal rates (Harrison et al, 1976). Removal through chlorination should not be viewed necessarily as a desirable effect. Chlorination does not necessarily remove the PAH moiety. Rather, chlorine can react with PAHs synthesizing new compounds which most likely remain in solution. Presently, little is known about these new compounds or their character; however, some data on the reaction products are listed in Table IX.

Activated Carbon

The effective removal of organic compounds, including PAHs, by activated carbon is dependent on the type of carbon used and its physical properties as well on specific compounds being adsorbed. In addition, removal is dependent on both kinetic and equilibrium considerations. The contact time as well as the concentrations of specific PAHs are of prime importance (Hansen, 1979). The traditional perception has been that only activated carbon can significantly reduce PAH concentrations in water. Borneff's work is among the most widely quoted in support of this contention. In a paper by Borneff and Fischer (1962), activated carbon filtration is credited with 99% removal of PAHs from water filtered by prior seepage through river bank soil. Again, in laboratory testing, 99% removal of PAHs (300 ug/l) was demonstrated for 10 types of activated carbon (Borneff, 1978).

Other authors have attributed efficient removal of PAHs during treatment to the use of activated carbon. This is evident in a paper by Lewis (1975). Comparing from Table XI the PAH concentrations in the

"Colwick F3" sample (raw water after biological pretreatment, copper coagulant, sedimentation and rapid sand filtration) to the Colwick G1 sample (F3 water after activated carbon filtration), Lewis viewed the reduction from 11 ng/l to 1.2 ng/l for 5 PAHs as confirmation that activated carbon is the only effective agent in reducing levels of PAHs. While the relative reduction of F3 to G1 is 90%, the absolute reduction (9.8 ng/l) of the PAHs, when compared to the original amount of PAHs in the raw water "Colwick B" (480 ng/l), is only 2%. Colwick F3, conventional treatment, apparently affords a 98% reduction, due to the removal of the PAH enriched particulates. From a recent paper, (Saxena et al, 1978), it has been inferred that the most effective removal process involves the use of a two stage activated carbon treatment. The data in Table XII does not convincingly support this contention, but in fact, is consistent with removal by conventional treatment. A comparison of Pittsburgh (2 stage treatment PAC addition, then GAC filter bed) with Philadelphia (conventional treatment) shows that for 3 of the 6 PAHs, the conventional treatment alone was more effective. In reality, there is probably little difference in effectiveness between the two treatment processes for PAH reduction, if initial concentrations and analytical precision are considered.

Use of activated carbon for the removal of PAHs present at very low nanogram-per-liter concentrations appears to have limited applicability. As an example, one can compare the raw and finished water data for Appleton, WI (GAC filtration) and Champaign, IL (no activated carbon added) (Table XIII). For all but one of the 6 PAHs, the percent removal of the noncarbon treatment was equal or greater than that of the carbon treated water.

Table XI
PAHs in Treatment Plant Water (ng/l)^a

Source	PAHs in Suspended Solids ^b					PAHs in Solution ^c				
	F1	B(a)P	IP	B(k)F	B(ghi)P	F1	B(a)P	IP	B(k)F	B(ghi)P
River Trent Colwick-B (Raw Water)	133.0	96.0	75.0	47.0	111.0	16.0	0.5	0.5	0.5	0.8
Colwick-F3 (Finished Water)	No Suspended Matter					9.3	0.3	0.6	0.4	0.6
Colwick-G1 (Granular Activated Carbon Filtered Water)	No Suspended Matter					0.8	0.2	d	d	0.2

a Lewis, 1975.
 b The particulate matter filtered from water sample.
 c Filtrate of water sample.
 d Present at less than quantitation limits.

Table XII
Comparison of Conventional and Two Stage Activated Carbon Treatment^a

Compound	Concentration, ng/l			
	Pittsburgh, PA ^b		Philadelphia, PA ^c	
	Raw	Finished	Raw	Finished
Fluoranthene	408.3	d	114.3	8.9
Benzo(j)fluoranthene	35.7	0.3	42.6	d
Benzo(k)fluoranthene	19.1	0.2	33.0	d
Benzo(a)pyrene	42.1	0.4	41.1	0.3
Indeno(1,2,3-cd)pyrene	60.4	1.2	72.4	1.7
Benzo(ghi)perylene	34.4	0.7	48.4	4.0

^a Saxena, et.al., 1977.
^b Two stage activated carbon treatment; powdered A.C. - then granulated A.C. filtration (~ 30-40 min empty bed contact time)
^c Conventional treatment.
^d Not detected, limits ranging from 0.1 - 4.6 ng/l.

Table XIII
Comparison of Carbon Treated Versus Non-Carbon Treated Water^a

Compound	Concentration, ng/l			
	Appleton, WI ^b		Champaign, IL	
	Raw	Finished	Raw	Finished
Fluoranthene	c	c	c	c
Benzo(j)fluoranthene	0.7	0.4	0.6	0.3
Benzo(k)fluoranthene	0.5	0.2	0.7	0.3
Benzo(a)pyrene	0.6	0.4	c	c
Indeno(1,2,3-cd)pyrene	0.9	1.4	1.9	0.9
Benzo(ghi)perylene	4.3	3.7	3.7	1.3

a Basu, et.al., 1978.
b GAC Filtration - Filtersorb 400 (~10 min empty bed contact time)
c Not detected.

In another series of experiments, under more controlled circumstances, finished waters were passed through a sand replacement filter or pilot column of granulated activated carbon, Table XIV (Sorrell et al, 1979). The resulting effluents showed a maximum reduction in PAHs of only 6 ng/l, where the influent was less than 23 ng/l. However, when the influent was at 80 ng/l, the PAH concentration was lowered to 16 ng/l, a reduction of 64 ng/l (80%). These results seem to support the contention that activated carbon is "uneconomical" for the removal of PAHs at concentrations of less than 30 ng/l (Borneff, 1977).

In an additional study, Borneff (1978) presented the results for PAH removal at two water treatment plants. At the Wiesbaden-Schierstein plant, water which was pretreated by sedimentation and flocculation was passed through a granular activated carbon column of Norit PKH (1-3 mm). The water at the head of the column was found to contain 70 ng/l of PAHs (probably the total for 8 PAHs). Upon exiting the column, the concentration was only 8 ng/l, or 90% reduction. A plant on the Danube river using pretreated water (35 ng/l PAHs) afforded only a 12% reduction of PAHs after passage over activated carbon at a flow rate of 12.7 m/h. From these studies it would appear that activated carbon is not always appropriate for the removal of PAHs at low concentrations in finished waters. These same studies, however, demonstrate that GAC can provide an effective barrier against unexpectedly high levels of PAHs.

Distribution System

Regardless of the effectiveness of the treatment techniques used in removing PAHs, the finished water can become recontaminated during containment in storage tanks or in transit through pipes with a coal tar

Table XIV

Concentrations (ng/l) of PAHs in Carbon Column Influent (Inf) and Effluents (Eff)^a

Compound	Miami, FL		Seattle, WA		Jefferson Parish, LA			
	Inf	Eff ^c	Inf	Eff ^c	Inf	Eff ^d	Inf	Eff ^e
Phenanthrene	11	6	6	8	14	10	52	14
Fluoranthene	<3	<2	<5	<2	4	6	11	<2
Pyrene	<4	<2	<4	<3	4	3	17	2
1-Methyl Pyrene	<1	<1	<1	<1	<2	<2	<2	<2
Anthracene	b	b	b	b	<2	<2	<2	<2
Chrysene	<1	<1	<1	<1	<2	<2	<2	<2
Benzo(a)anthracene	1	<1	1	<1	<2	<2	<2	<2
Perylene	<1	<1	<1	<1	<2	<2	b	<2
Benzo(e)pyrene	<1	<1	<1	<1	<2	<2	<2	<2
Benzo(a)pyrene	<1	<1	<1	<1	<2	<2	<2	<2
Benzo(ghi)perylene	<1	<1	<1	<1	<2	<2	b	<2
Benzo(b)fluoranthene	<1	<1	<1	<1	<2	<2	<2	<2
Benzo(k)fluoranthene	<1	<1	<1	<1	<2	<2	<2	<2
Dibenzo(a,h)anthracene	<1	<1	<1	<1	<2	<2	<2	<2
Indeno(1,2,3-cd)pyrene	<1	<1	<1	<1	<2	<2	<2	<2
Total	12	6	7	8	22	19	80	16
<p>a Sorrell, et.al., 1979.</p> <p>b Not analyzed.</p> <p>c Virgin carbon (Filtersorb 400) used in a pilot column with 19 minute empty bed contact time.</p> <p>d Exhausted carbon (Westvaco WVG) used in a sand replacement filter with an average empty bed contact time of 18 minutes.</p> <p>e Fresh carbon (Filtersorb 400).</p>								

base lining (Goldfarb et al., 1979, Borneff and Kunte, 1965). To some extent, this is also true of pipes lined with asphaltic base materials. A laboratory study (Sorrell, et al., 1977) has demonstrated leaching of PAHs (70 ng/l, mostly phenanthrene) from pipe with an asphalt base coating.

For coal tar based coatings, a recent study (DWRD, 1980) has found nanogram to microgram per liter concentrations in contacted water. In this study, 4 glass plates, coated with coal tar enamel, were placed in a TLC chamber affording a high surface area to volume ratio. Tap water was allowed to flow through the system at a measured rate. Prior to sampling the tap water was stopped for 3 days, then continued after sampling. The results in Table XV at 25 and 165 days show significant leaching of the target compounds in both samples, indicating that under the test conditions leaching was likely to continue for a long period of time. It should be noted that these laboratory studies cannot be used to predict concentration of PAHs under real distribution system conditions, even when the same type of coating is in use.

The magnitude of contamination in distribution systems will be determined in part by the age of the coating, contact time of the water, surface area to water volume, the type of coating used, appropriate application, deposition of carbonate, etc. The data base for PAHs leaching from distributed water systems located in the United States is, to date, limited. The supplies listed in Table XVI do not demonstrate a consistent trend with regard to contamination and the type of lining used. Similar results have been reported by other researchers (Crane et al., 1978, Basu and Saxena, 1977).

Table XV

Compound	Plate Test Concentrations ^{a,b} (ng/l)	
	25 days ^c	165 days ^c
Phenanthrene	230,000	290,000
Fluoranthene	34,000	46,000
Pyrene	20,000	27,000
1-Methylpyrene	< 1,600	< 290
Anthracene	23,000	14,000
Chrysene	1,000	1,300
Benzo(a)anthracene	1,100	1,300
Perylene	Present	Present
Benzo(e)pyrene	Present	Present
Benzo(a)pyrene	78	110
Benzo(ghi)perylene	< 30	< 40
Benzo(b)fluoranthene	170	140
Benzo(k)fluoranthene	100	89
Dibenzo(a,h)anthracene	< 10	3
Indeno (1,2,3-cd) pyrene	< 58	< 50

a DWRD (1980)

b Plate contact area/volume water was $\sim 838 \text{ cm}^2/\text{l}$

c Temperature of water at 25 day $\sim 18^\circ\text{C}$; at 165 days $\sim 20^\circ\text{C}$.

Table XVI

Concentration (ng/l) of PAHs in Finished and Distributed Waters^a

Compound	Standish, ME ^b		Ludlow, MA ^b		Columbus, OH ^c		Portland, OR ^{b,c}		Seattle, WA ^b		Colorado Springs, CO ^b	
	Fin	Dist ^d	Fin	Dist ^d	Fin	Dist ^{d,f}	Raw	Dist ^{e,g}	Fin	Dist ^e	Fin	Dist ^e
Ph	5	57	2	3	3	17	8	3300	2	32	3	29
F1	2	10	1	1	1	13	4	640	3	8	2	6
Pyr	1	5	1	1	<1	8	6	340	2	2	<1	<1
1-MP	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
An	<1	<1	<1	<1	--	--	--	--	<1	<1	<1	<1
Ch	<1	<1	<1	<1	<1	4	<1	26	<1	<1	<1	<1
B(a)A	<1	<1	<1	<1	<1	3	<1	2	<1	<1	<1	<1
Per	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
B(e)P	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
B(a)P	<1	<1	<1	<1	<1	--	<1	<1	<1	<1	<1	<1
B(ghi)P	<1	<1	<1	<1	<1	2	<1	<1	<1	<1	<1	<1
B(b)F	<1	<1	<1	<1	<1	4	<1	3	<1	<1	<1	<1
B(k)F	<1	<1	<1	<1	<1	3	<1	<1	<1	<1	<1	<1
DiB(ah)A	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
IP	<1	<1	1	1	<1	<4	<1	<1	<1	<1	<1	<1
Total	8	72	5	6	4	54	18	4300	7	42	5	35

- a < Indicates that the compound may or may not have been present at less than this concentration
b Zoldak, 1978
c Sorrell, et al., 1979
d Asphalt lining
e Coal tar lining
f Sediment present in water sample
g Taken at the end of a low demand 24" transmission line

Toxicology and Present Standards

From a human toxicological (carcinogenic) viewpoint, there appears to be scant data upon which to base a maximum contaminant level (MCL) for drinking water. The U.S. National Academy of Sciences (1977) has only attempted to evaluate one PAH, benzo(a)pyrene indicating the available data were insufficient for establishing risk estimates.

Presently, the most widely quoted standard for PAHs is that of the World Health Organization which set a 200 ng/l maximum permissible concentration for the sum of six PAHs (fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene) in drinking water (WHO, 1971). The six PAHs were chosen because they could be easily analyzed and not necessarily because of their toxicological properties, as only three of the six PAHs are thought to possess carcinogenic characteristics.

The philosophy of this standard is that tap water derived from surface water should contain no more PAHs than the tap water derived from ground water (Crathorne and Fielding, 1978). Using the data of Borneff and Kunte, the average figure for total (6) PAHs in tap water derived from ground water was 100 ng/l. A factor of 2 was added to account for natural variation, hence 200 ng/l.

Andelman and Suess (1970) discussed the concept that carcinogen consumption from water should not exceed 1/10 that from urban air. This relates to about 17 ng/l of carcinogenic material from water. But again it is based on a "natural" background concept and without benefit of toxicological data.

Conclusions

In addition to the requirement for more toxicological data, further investigation to establish the scope of PAH contamination in U.S. waters (raw, finished, and distributed) seems appropriate. While present data would indicate conventional treatment is capable of reducing PAH concentrations well below the WHO limits, little information is available as to the products resulting from chlorination or their toxicology. Even if research proved these by-products to be of no concern, deterioration of the finished water quality can occur within the distribution system. The primary sources of such contamination would be from coal-tar or asphaltic materials used to line pipes and storage tanks.

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