Implications of Treating Water Containing Polynuclear Aromatic Hydrocarbons with Chlorine: A Gas Chromatographic-Mass Spectrometric Study

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The products of aqueous chlorination reactions of 1-methylnaphthalene, fluorene, dibenzofuran, anthracene, phenanthrene, 1-methylphenanthrene, fluoranthene, and pyrene have been determined. The conditions employed for these reactions approximated those that might be encountered in water treatment facilities. Reactions at pH > 6 tended to produce oxygenated products (epoxides, phenols, quinones, etc.), and reactions at pH < 6 tended to produce both oxygenated (quinones) and chlorinated products.

The use of chlorination as the predominant technique for water renovation and disinfection has been questioned because of the reaction of active chlorine species with organic compounds present in the water to form products which may be biologically harmful (1-3). These reactions may occur at the site of chlorine addition as well as throughout a water distribution system (4). Polynuclear aromatic hydrocarbons (PAH) have been suggested as the precursors to at least a portion of the mutagens produced in some chlorination processes (4). The levels of these ubiquitous PAH compounds may be increased by the presence of coal tar coatings inside pipes and water storage tanks (5).

In order to provide further insight into the possible role of PAH in chlorine-induced mutagen formation, this laboratory has continued the study of the aqueous chlorination chemistry of PAH (6, 7). The present report describes a detailed study of the product distributions of several PAH compounds which were chosen for study based on their previous identification in drinking water (8). A related study in these laboratories of the reaction kinetics and mechanisms for the aqueous chlorination of phenanthrene, fluorene, and fluoranthene will be reported elsewhere.

Experimental Procedure

Twelve liters of water were treated with chlorine gas, and an appropriate amount of sodium hydroxide was added to achieve the desired pH. A solution of the PAH in acetonitrile (40-800 ml, specific conditions in Tables) was added to initiate the reaction which was monitored by HPLC. For high pH solutions, the pH was maintained by periodic addition of NaOH. To this, 2.5-3 equivalents (based on the total chlorine concentration) of dimethyl sulfoxide or sodium thiosulfate were added to terminate the reaction. In some cases, the reactant solution was acidified with sulfuric acid in order to suppress ionization of acidic products. The solution was then forced through two 7 × 50 mm stainless steel adsorption columns connected in series. The first column contained C-18 Porasil B (37-75 μm, Waters Asso-
ciates), and the second contained XAD-2 (100 μm, Rohm and Haas). Reaction products which were adsorbed were later removed by elution of the column train with acetonitrile and then with methylene chloride. Some separation of these products was observed during the elution process. The various fractions collected were then checked for product content by HPLC and concentrated under a nitrogen stream prior to analysis by gas chromatography-mass spectrometry (GC/MS). Portions of fractions suspected of containing acidic compounds were methylated with diazomethane.

**Standards**

The following compounds were purchased, checked for purity, and, where necessary, purified by recrystallization, sublimation, and/or preparative reversed phase liquid chromatography: phenanthrenequinone, 9-chlorophenanthrene, 9-fluorenone, 1-chloropyrene.

The following compounds were prepared according to literature methods: trans-9,10-dihydro-9,10-dihydroxyphenanthrene (9), 2-chlorodibenzo[2,3]furan (10), 2,8-dichlorodibenzo[2,3]furan, (10), phenanthrene-9,10-oxide, (11), 2,3-fluoranthenedione (12), 3-fluoranthenol (13), 2-chlorofluorenone (14), 3-chlorofluoranthene (14), 4-pyrenol (15), 9-fluorenone-1-carboxylic acid (16), 4,5-pyrene-1-carboxylic acid (17), cis-4,5-dihydro-4,5-dihydroxyphenanthrene (18), dichloropyrene (19, 20), 1,6-1,8-pyrene-dione (21), and 4,5-phenanthrendicarboxylic acid anhydride (22).

9-Phenanthrenol was prepared by the rearrangement of phenanthrene-9,10-oxide with base. Diisopropylamine (0.476 g, 0.0047 mmole) and n-butyl-lithium (3.23 ml of 1.6M solution in hexane, 0.0052 mole) were combined in tetrahydrofuran (THF) at −78°C under N₂. A slurry of phenanthrene-9,10-oxide (0.911 g in THF, 0.0047 mole) was added by syringe and the mixture was then allowed to warm slowly overnight. Sulfuric acid (1N) was added, and the mixture was twice extracted with benzene and the combined extracts were dried with magnesium sulfate and evaporated in a rotary evaporator at 30°C. Tan crystals (0.844 g, 92%) resulted with mp 144–147°C. Recrystallization from benzene gave tan crystals, mp 149-151°C (lit. mp 151–152°C) (23). IR(KBr) showed the absence of phenanthrenequinone. This phenol undergoes rapid autoxidation to phenanthrenequinone (23), at such a rate as to preclude the preparation of pure solutions. The generation of an HPLC standard curve required correction for the amount of quinone present.

9,10-Dichlorophenanthrene was prepared by the chlorination of phenanthrene. Methylene chloride (100 ml) and commercial bleach (100 ml) were combined in a closed container and the pH of the aqueous layer adjusted to 4 with phosphoric acid (11). The total chlorine content of the two layers was determined by iodometric titration to be 0.03 M. Phenanthrene (0.85 g, 0.0048 mole) was added and the mixture stirred at room temperature for 5 hr. The organic layer was then removed, washed with water and saturated with sodium thiosulfate solution, dried over magnesium sulfate and evaporated to yield a yellow solid (80%). Recrystallization from methanol and again from acetonitrile gave tan crystals of mp 157.5-159°C (lit. mp 158-160°C) (19); NMR (CDCl₃) δ 7.6-8.1 (m, 4H), 8.4-9.0 (m, 4H).

2,7-Dichlorofluorene was prepared from the bis-diazonium salt. 2,7-Diaminofluorene (1.0 g, 1 mmole, Aldrich Chemical Co.) was placed into 4 ml of water and added to 11 ml of 4.4N hydrochloric acid. Sodium nitrate (0.155 g, 2.2 mmole) in 4 ml of water was then added and the resulting mixture was stirred for 1.5 hr at 20°C. This mixture was then added to a slurry of cuprous chloride (0.385 g, 4.3 mmole) in 8 ml of water. After 4 hr at 50°C the resulting solid was removed, taken up into methylene chloride and washed with 1N hydrochloric acid, 1N sodium hydroxide, and water. The organic layer was then dried over magnesium sulfate and evaporated. Recrystallization of the solid from hexane and then from methanol gave 2,7-dichlorofluorene, a white solid of mp 126°C (lit. mp 128°C) (25); NMR (CDCl₃) δ 3.9 (s, 2H), 7.2-7.9 (m, 6H).

4,5-Phenanthrendicarboxylic acid was prepared from the corresponding pyrene-dione by a procedure similar to that reported for oxidation of fluoranthenequinone (16). 4,5-Pyrene-dione (0.045 g, 0.195 mmole) was dissolved in 25 ml of tetrahydrofuran, and 10 ml of 30% H₂O₂ was added. After stirring overnight, the solution was acidified to pH 2 with hydrochloric acid and the product was extracted with methylene chloride, dried, and evaporated. Crystals (0.018, 35% yield) formed and were recrystallized from methanol: mp = 256°C (lit. mp = 258°C) (22). Mass spectrum of product after diazomethane treatment: m/e = 294(10), 235(100), 220(46).

**Instruments and Apparatus**

The gas chromatograph-mass spectrometer (GC-MS) was a Hewlett-Packard 5993B quadrupole, EI-70 eV equipped with an Avondale B capillary inlet and a 21 MX-E computer (ANSWER software). The GC/MS interface was modified to allow the entire effluent from a fused silica capillary columns to be drawn into the mass spectrometer. The column was either a 25 m (0.32 mm ID) SE-54 (siloxane, Hewlett-Packard) or a 15m (0.32 ID) poly methyl (5% phenyl) siloxane (J & W Scientific). Splitless injections were employed with 5-8 psi head pressure and 2 ml/min He carrier flow. A typical temperature program was 70 to 310°C at
Results and Discussion

Equilibria Considerations

The predominant chlorine-containing species in aqueous chlorine solutions are HOCl, OCl\(^-\), Cl\(^-\), Cl\(_2\), and Cl\(_3^-\) (26). The relationships between the species are summarized by Eqs. (1), (2) and (3) (27–29). The OCl\(^-\) and HOCl concentrations are significant at pH greater than ~6 and the HOCl, Cl\(_2\) and Cl\(_3^-\) concentrations are significant at pH less than ~6.

\[
\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^- 
\]

(1)

with

\[
K_{\text{HOCl}} = 2.62 \times 10^{-8} \text{ at } 20°C.
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- 
\]

(2)

with

\[
K_{\text{Cl}^-} = 3.38 \times 10^{-4} \text{ at } 20°C.
\]

\[
\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_3^-(3)
\]

(3)

with

\[
K_{\text{Cl}^-} = 0.19 \text{ at } 25°C.
\]

Table 1. Products of 1-methylnaphthalene reactions.

| Proposed structure | Relative retention time (GC) | Molecular ion, m/z | Amt present | pH 3\(^b\) | pH 8\(^c\) | m/z (relative abundance) |
|--------------------|-------------------------------|-------------------|-------------|----------|---------|------------------------|
| C\(_9\)H\(_8\)O\(_2\) | 1.061 148 | — | Minor | 148 (6), 133 (15), 120 (4), 105 (100), 91 (18), 77 (89) |
| C\(_9\)H\(_8\)O\(_2\) | 1.106 148 | — | Trace | 148 (7), 133 (71), 105 (100), 77 (55) |
| OH | 1.458 158 | Minor | — | 158 (100), 143 (2), 141 (4), 130 (16), 129 (38), 128 (29), 127 (16), 115 (15), 103 (8), 102 (10) |
| OH | 1.556 158 | Minor | — | 158 (100), 157 (70), 143 (1), 141 (3), 130 (13), 129 (30), 128 (39), 127 (18), 115 (15), 103 (6), 102 (5) |
| O | 1.355 172 | Minor | — | 172 (100), 157 (5), 144 (19), 127 (16), 117 (8), 116 (54), 115 (77), 90 (56), 89 (54), 63 (29) |
| (OH)\(_2\) | 1.442 174 | Minor | Trace | 174 (10), 159 (100), 131 (39), 105 (12), 103 (28), 77 (33) |
| Cl | 1.358 176 | Minor | — | 176 (64), 178 (26), 141 (100), 138 (37), 115 (40) |
| Cl \(_2\) | 1.376\(^d\) 176 | Minor | Major | 176 (65), 178 (24), 142 (12), 141 (100), 139 (36), 115 (34) |
| Proposed structure | Relative retention time (GC)<sup>a</sup> | Molecular ion, m/z | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|----------------------------------------|-------------------|---------------|---------------|-------------------------|
| Unknown            | 1.587                                  | ?                 | —             | Minor         | 181 (92), 183 (32), 147 (100), 91 (34), 90 (43), 89 (55), 70 (49) |
| [Image of structure] | 1.541<sup>e</sup>                      | 186               | —             | Trace         | 186 (47), 155 (100), 127 (60) |
| [Image of structure] | 1.414                                 | 188               | —             | Minor         | 188 (72), 173 (100), 161 (28), 160 (87), 132 (19), 131 (43), 105 (34), 104 (21), 103 (31), 89 (79), 77 (51) |
| [Image of structure] | 1.511                                 | 188               | —             | Minor         | 188 (90), 160 (13), 132 (9), 131 (8), 119 (76), 104 (22), 103 (100), 91 (70), 90 (70), 89 (71), 77 (59) |
| [Image of structure] | 1.599                                 | 192               | Minor         | —             | 192 (100), 194 (37), 177 (1), 157 (85), 129 (38), 128 (75), 127 (61), 126 (21), 102 (24), 77 (36), 64 (30), 63 (54) |
| [Image of structure] | 1.880                                 | 192               | Minor         | —             | 192 (100), 194 (37), 177 (2), 163 (20), 157 (46), 139 (17), 129 (53), 128 (22), 127 (55), 126 (18), 102 (17), 101 (15), 77 (29), 76 (21), 75 (27), 74 (23), 63 (50) |
| [Image of structure] | 1.897                                 | 192               | Minor         | —             | 192 (100), 194 (37), 177 (2), 165 (9), 163 (22), 157 (42), 129 (38), 128 (55), 127 (45), 126 (15) |
| Unknown            | 1.582                                  | ?                 | —             | Minor         | 195 (100), 197 (39), 180 (8), 178 (7), 169 (6), 143 (4), 131 (24), 115 (8), 103 (37), 89 (7), 77 (24) |
| [Image of structure] | 1.728                                 | 206               | Minor         | —             | 206 (71), 208 (25), 180 (8), 179 (8), 178 (17), 163 (8), 165 (2), 150 (20), 150 (17), 143 (22), 126 (8), 124 (23), 115 (100), 114 (18), 89 (49), 87 (22), 86 (22), 75 (17), 74 (18), 73 (14), 63 (52) |
| [Image of structure] | 1.496                                 | 208               | —             | Minor         | 208 (5), 190 (9), 175 (26), 167 (34), 165 (100), 147 (15), 145 (12), 129 (12), 115 (18) |
| Cl(OH)<sub>2</sub> | 1.481                                  | 208               | Major         | —             | 208 (10), 210 (4), 182 (16), 180 (40), 167 (16), 165 (41), 145 (100), 144 (23), 116 (17), 115 (40), 102 (41), 101 (43), 77 (25), 75 (50) |
| Cl(OH)<sub>2</sub> | 1.772                                  | 208               | Minor         | —             | 208 (8), 210 (4), 195 (30), 193 (76), 173 (100), 167 (8), 165 (19), 157 (24), 155 (11), 129 (15), 128 (10), 127 (17), 115 (15), 105 (50), 102 (35), 101 (36) |
| Proposed structure | Relative retention time (GC)a | Molecular ion, m/z | Amt present | pH 3b | pH 8c | m/z (relative abundance) |
|-------------------|-------------------------------|-------------------|-------------|-------|-------|-------------------------|
| Cl (OH)2          | 1.784                         | 208               | Minor       | Minor | 208 (11), 210 (4), 195 (29), 193 (80), 173 (100), 167 (8), 165 (22), 157 (24), 155 (11), 129 (15), 128 (12), 127 (18), 115 (20), 105 (44), 102 (32), 101 (29) |
| Cl (OH)2          | 1.797                         | 208               | Minor       |       | 208 (72), 210 (20), 182 (6), 180 (14), 167 (19), 165 (25), 155 (17), 154 (27), 153 (36), 152 (88), 145 (34), 124 (71), 117 (44), 115 (11), 103 (18), 89 (87) 62 (100) |
| Cl (Cl)2          | 1.674                         | 210               | Major       | Trace | 210 (57), 212 (34), 177 (35), 175 (100), 149 (14), 139 (70), 113 (8) |
| Cl (Cl)2          | 1.686                         | 210               | Major       | Trace | 210 (60), 212 (35), 177 (33), 175 (100), 151 (4), 149 (14), 139 (56), 113 (6) |
| Cl (Cl)2          | 1.712                         | 210               | Minor       | Trace | 210 (43), 212 (24), 177 (33), 175 (100), 139 (38) |
| CH2Cl             | 1.804                         | 210               | Minor       |       | 210 (60), 212 (33), 177 (37), 175 (100), 149 (16), 139 (52) |
| CH2OH             | 1.812                         | 222               | —           | Trace | 222 (63), 224 (23), 223 (16), 221 (28), 207 (8), 205 (10), 187 (23) |
| Cl (OH)3          | 1.694                         | 224               | —           | Major | 224 (3.8), 226 (1.4), 209 (9), 189 (18), 183 (5), 181 (16), 173 (13), 171 (23), 161 (100), 149 (11), 147 (24), 143 (35), 91 (39), 89 (52), 77 (74) |
| HO (Cl)3          | 1.916                         | 226               | Minor       |       | 216 (100), 228 (56), 211 (4), 209 (5), 193 (29), 192 (34), 191 (72), 173 (11), 165 (17), 164 (25), 163 (45), 162 (52), 137 (4), 128 (51), 127 (85), 126 (88), 113 (8) |
| (Cl)2 (OH)2       | 1.855                         | 242               | —           | Minor | 242 (15), 244 (8), 209 (4), 207 (16), 181 (36), 179 (92), 171 (37), 143 (18), 116 (38), 115 (100), 89 (38) |
| HO (Cl)3          | 1.820                         | 244               | Minor       |       | 244 (4), 246 (3), 211 (22), 210 (14), 209 (54), 208 (16), 193 (25), 192 (17), 191 (30), 180 (15), 179 (23), 173 (100), 165 (30), 163 (39), 162 (23), 157 (13), 145 (22), 142 (42), 129 (20), 128 (44), 127 (42), 126 (18), 117 (17), 116 (18), 115 (62) |
| Cl (Cl)3          | 1.945                         | 244               | Minor       |       | 244 (50), 246 (49), 211 (68), 210 (20), 209 (100), 185 (9), 183 (13), 175 (29), 173 (67), 137 (22) |
| Cl (Cl)3          | 1.961                         | 244               | Minor       |       | 244 (55), 246 (56), 211 (70), 209 (100), 185 (11), 183 (18), 175 (28), 173 (69), 137 (25) |
An anticipated difference in reaction kinetics and reaction mechanisms between low and high pH chlorination reactions of PAH has already been noted (30). In the present study, therefore, the product distributions for each compound were determined at both pH 3 and pH 8 in order to insure the maximum probability for observing products formed by all reactive chlorine species.

**Products**

The products observed are listed in Tables 1–8 along with their mass spectral data. In most cases the product distributions were determined after the PAH ($\sim 10^{-6} M$) was allowed to react with $\sim 10^{-3} M$ chlorine for five to seven half-lives (specific conditions are included in the tables). A small amount of acetonitrile (1 to 8%) was used in many reactions to provide sufficient quantities of PAH products for analysis and to minimize the formation of PAH crystals during a reaction. The use of such small amounts of this organic solvent did not appear to alter the product distribution based on chromatographic comparison with reactions in the absence of acetonitrile. In contrast, reaction solutions containing crystalline PAH material tended to result in the formation of only chloro products rather than both the chloro and oxygenated products observed in homogeneous solutions.

Reactions at high pH tended to produce oxygenated products while those at low pH tended to give both oxygenated and chlorinated products. The predominant product types included mono- and dichlorosubstituted compounds, quinones, phenols, carboxylic acids, and an epoxide. Minor compound types included chlorohydrins and dihydrodiols. A detailed mechanistic investigation of phenanthrene suggested the formation of an arene oxide as the key intermediate in interpreting the product distribution.

Free-radical substitution on the methyl groups of 1-methylphenanthrene and 1-methylnapthalene and the benzylic carbon of fluorene was not extensive. This type of reaction which results in the formation of benzylic halides and alcohols has previously been reported for some chlorination reactions (31). Benzylic alcohols can be distinguished from ring-substituted

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**Table 1. (continued)**

| Proposed structure | Relative retention time (GC)* | Molecular ion, m/z | Amt present | pH 3b | pH 8c | m/z (relative abundance) |
|--------------------|-------------------------------|-------------------|------------|-------|-------|-------------------------|
| C_{12}H_{13}O_3Cl*  | 2.294                         | 254               | Minor      |       |       | 254 (26), 256 (10), 241 (34), 239 (100), 218 (10), 211 (9), 209 (19), 208 (17), 207 (65), 206 (32), 203 (7), 195 (13), 193 (11), 175 (15), 171 (26), 163 (16), 159 (37), 147 (65), 143 (21), 135 (15), 115 (42), 105 (46) |
| C_{12}H_{11}O_3Cl* | 2.294                         | 254               | Minor      |       |       | 254 (26), 256 (10), 241 (34), 239 (100), 218 (10), 211 (9), 209 (19), 208 (17), 207 (65), 206 (32), 203 (7), 195 (13), 193 (11), 175 (15), 171 (26), 163 (16), 159 (37), 147 (65), 143 (21), 135 (15), 115 (42), 105 (46) |
| C_{12}H_{10}O_3Cl* | 2.370                         | 260               | Minor      |       |       | 260 (100), 262 (36), 261 (55), 259 (81), 246 (0.4), 244 (3), 233 (4), 231 (10) |
| C_{12}H_{10}O_3Cl* | 2.441                         | 260               | Minor      |       |       | 260 (100), 262 (36), 261 (49), 259 (86), 233 (6), 231 (10) |

*Reference = 1-methylnaphthalene.

b$\text{pH} = 3.0$, [1-methylnaphthalene] $= 2 \times 10^{-5}$ [total chlorine] $= 1 \times 10^{-3}$, 96 hr required for 3 half-lives.

c$\text{pH} = 8.0$, [1-methylnaphthalene] $= 2 \times 10^{-5}$ [total chlorine] $= 1 \times 10^{-3}$, 1 hr required for 2 half-lives.

dRelative retention time (GC) and mass spectrum identical to those of an authentic standard.

eDerivatized with diazomethane prior to GC/MS analysis.
### Table 2. Products of fluorene reactions.

| Proposed structure | Relative retention time (HPLC) | Molecular ion, m/z | Amt present | pH 3 | pH 8 | m/z (relative abundance) |
|--------------------|-------------------------------|-------------------|-------------|------|------|--------------------------|
|                    |                               |                   |             |      |      |                          |
| ![Fluorene](image)  | 0.903                         | 180               | -           |       | ~ 2% |                          |
| ![Fluorene](image)  | 1.097                         | 200               | 44%         | 200(44), 202(14), 166(29), 165(100), 164(43), 163(58) |
|                    | 1.184                         | 234               | 10%         | 234(20), 236(18), 201(50), 199(100), 165(20), 164(24), 163(54) |

*Reference = fluorene.

bPH = 3.05, [fluorene] = 1.38 x 10^-4, [total chlorine] = 4.21 x 10^-4, 360 min required for 4.5 half-lives.

pH = 7.70, [fluorene] = 1.38 x 10^-4, [total chlorine] = 4.01 x 10^-4, 7 days required for 2 half-lives.

HPLC retention time and m/z identical to those of an authentic standard.

The percent yields were determined by HPLC utilizing authentic compounds as standards.

Relative retention time and mass spectrum identical to those of an authentic standard.

### Table 3. Products of dibenzofuran reactions.

| Proposed structure | Relative retention time (HPLC) | Molecular ion, m/z | Amt present | pH 3 | pH 8 | m/z (relative abundance) |
|--------------------|-------------------------------|-------------------|-------------|------|------|--------------------------|
|                    |                               |                   |             |      |      |                          |
| ![Dibenzofuran](image) | 1.168                         | 202               | Trace       | 202(100), 204(50), 175(6), 173(10), 167(7), 139(61) |
| ![Dibenzofuran](image) | 1.190                         | 202               | Minor       | 202(100), 204(45), 175(3), 173(8), 167(4), 139(62) |
| ![Dibenzofuran](image) | 1.212                         | 202               | Major       | 202(100), 204(40), 175(3), 173(5), 167(3), 139(45) |
| ![Dibenzofuran](image) | 1.225                         | 202               | Minor       | 202(100), 204(45), 175(3), 173(6), 167(2), 139(43) |
| ![Dibenzofuran](image) | 1.389                         | 236               | Minor       | 236(100), 238(53), 203(4), 201(6), 175(33), 173(81), 147(11), 138(37), 137(46) |
| ![Dibenzofuran](image) | 1.405                         | 236               | Major       | 236(100), 238(53), 203(2), 201(5), 175(23), 173(55), 147(5), 138(22), 137(27) |
| ![Dibenzofuran](image) | 1.414                         | 236               | Minor       | 236(100), 238(54), 203(4), 201(7), 175(37), 173(93), 147(10), 138(38), 137(44) |

*Reference = dibenzofuran.

bPH = 3.04, [dibenzofuran] = 2 x 10^-5, [total chlorine] = 1 x 10^-3, 4 hr required for 4 half-lives.

pH = 8.0, [dibenzofuran] = 2 x 10^-5, [total chlorine] = 1 x 10^-3, less than 50% of starting material reacted in one week.

Relative retention time and mass spectrum are identical to those of an authentic standard.
Table 4. Products of anthracene reactions.

| Proposed structure | Relative retention time (GC) | Molecular ion, m/z | Amt present | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|-----------------------------|--------------------|-------------|-----------------|-----------------|--------------------------|
| ![OH](image)       | 1.094                       | 194                | Trace       | 194 (73), 165 (100), 163 (25), 83 (31), 62 (34) |
| ![OH](image)       | 1.123                       | 194                | Trace       | 194 (100), 165 (71) |
| ![OH](image)       | 1.182                       | 208                | Major       | 208 (48), 207 (16), 180 (72), 153 (10), 152 (74), 151 (40), 150 (23), 126 (12), 76 (100), 74 (56) |
| ![OH](image)       | 1.263                       | 210                | Minor       | 210 (75), 209 (22), 208 (15), 193 (8), 181 (100), 165 (33), 163 (20), 153 (22), 152 (8), 151 (24), 150 (11), 105 (33), 104 (19), 77 (83), 76 (89), 63 (35) |
| ![OH](image)       | 1.317                       | 246                | Minor       | 246 (52), 248 (28), 213 (24), 212 (5), 211 (6), 210 (10), 176 (100), 174 (45), 150 (17), 149 (10), 124 (10), 123 (25), 122 (18) |

<sup>a</sup>Reference = anthracene.
<sup>b</sup>pH = 3.0, [anthracene] = 1.99 × 10<sup>-6</sup>, [total chlorine] = 1.0 × 10<sup>-3</sup>, 30 min were required for 7 half-lives, 4% acetonitrile.
<sup>c</sup>pH = 8.0, [anthracene] = 1.99 × 10<sup>-6</sup>, [total chlorine] = 1.0 × 10<sup>-3</sup>, 30 min were required for 7 half-lives, 4% acetonitrile.
<sup>d</sup>Relative retention time and mass spectrum are identical to those of an authentic standard.

Table 5. Products of phenanthrene reactions.

| Structure | Relative retention time (HPLC)<sup>a</sup> | Relative retention time (GC)<sup>a</sup> | Molecular ion, m/z | Amt present | pH 3<sup>b,c</sup> | pH 8<sup>c,d</sup> | m/z (relative abundance) |
|-----------|---------------------------------------------|------------------------------------------|-------------------|-------------|-----------------|-----------------|--------------------------|
| ![OH](image) | 0.816                                       | —                                         | 194               | 88%<sup>f</sup> |                 |                 |                          |
| ![OH](image) | 0.816                                       | —                                         | 194               | 19%        | ~ 2%<sup>f</sup> |                 |                          |
| ![OH](image) | 0.726                                       | 1.291                                     | 208               | 32%        | 2%              | 208 (14), 180 (100), 152 (57), 151 (29), 150 (20) |
| ![OH](image) | —                                           | 1.080                                     | 210               | Minor      | 210 (2), 181 (100), 153 (15), 152 (39) |
### Table 5. (continued)

| Structure | Relative retention time (HPLC)* | Relative retention time (GC)* | Molecular ion, m/z | pH 3b,c | pH 8c,d | m/z (relative abundance) |
|-----------|-------------------------------|-------------------------------|-------------------|--------|--------|---------------------------|
| Cl        | 1.128                         | —                             | 212               | 34%    | —      | 212 (69), 214 (33), 177 (36), 176 (62), 174 (15), 88 (100), 75 (60) |
| HO        | 0.614                         | 1.235                         | 212               | 3%     | —      | 212 (20), 194 (22), 181 (62), 166 (66), 165 (100), 163 (11), 152 (25) |
| Cl        | 1.251                         | —                             | 246               | 7%     | —      | 246 (100), 248 (72), 212 (7), 211 (12), 210 (16), 177 (15), 176 (92), 175 (40), 174 (34) |
| COOH(CH₃) | —                             | 1.200                         | 270               | Minor  | 270 (4), 239 (4), 211 (100), 180 (8) |

*Reference = phenanthrene.

b pH = 3.09, [phenanthrene] = 8.25 x 10⁻⁷, [total chlorine] = 4.46 x 10⁻⁴, 20 min required for 6 half-lives.

c The per cent yields were determined by HPLC utilizing authentic compounds as standards.

d pH = 7.70, [phenanthrene] = 6.60 x 10⁻⁷, [total chlorine] = 7.73 x 10⁻⁴, 90 min required for 8 half-lives.

'HPLC retention time and A₂₅₄/A₈₀₀ identical to those of an authentic standard.

i Calculated from absorbance data at 254 and 280 nm.

j Relative retention time and mass spectrum are identical to those of an authentic standard.

k Proposed structure.

l Derivatized with diazomethane prior to GC/MS analysis.

### Table 6. Products of 1-methylphenanthrene reactions.

| Proposed structure | Relative retention time (GC)* | Molecular ion, m/z | Amt present | pH 3b | pH 8c | m/z (relative abundance) |
|--------------------|-------------------------------|-------------------|-------------|-------|-------|---------------------------|
| OH CH₃             | 1.188                         | 208               | Minor       | Major |        | 208 (100), 207 (22), 180 (19), 179 (39), 178 (44), 165 (68) |
| CH₃                | 1.197                         | 222               | Major       | Major |        | 222 (62), 194 (76), 165 (100), 163 (18) |
| HO OH CH₃          | 1.108                         | 224               | —           | Trace | 224 (27), 209 (49), 181 (9), 83 (100) |
| HO H CH₃           | 1.117                         | 226               | —           | Major | 226 (34), 208 (37), 195 (74), 180 (34), 179 (51), 176 (40), 176 (19), 165 (100), 152 (23) |
Table 6. (continued)

| Proposed structure | Relative retention time (GC) | Molecular ion, m/z | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|-----------------------------|--------------------|-----------------|-----------------|--------------------------|
| ![Structure 1](image1.png) | 1.125 | 226 | — | Minor | 226 (50), 209 (20), 208 (63), 207 (14), 195 (88), 181 (27), 180 (35), 179 (52), 178 (41), 176 (11), 165 (100), 152 (23) |
| ![Structure 2](image2.png) | 1.115 | 226 | Minor | — | 226 (87), 226 (22), 191 (100), 189 (78), 187 (19), 165 (16), 164 (12), 163 (17) |
| ![Structure 3](image3.png) | 1.293 | 242 | Minor | — | 242 (92), 244 (26), 207 (33), 179 (100), 178 (70), 176 (28) |
| ![Structure 4](image4.png) | 1.305 | 242 | Trace | — | 242 (100), 244 (27), 207 (52), 179 (77), 178 (64), 176 (30) |
| ![Structure 5](image5.png) | 1.217 | 260 | Minor | — | 260 (43), 262 (15), 244 (9), 242 (32), 231 (10), 229 (30), 226 (16), 225 (79), 215 (9), 213 (25), 207 (36), 195 (18), 194 (25), 179 (100), 178 (61), 176 (17), 165 (77), 163 (19), 152 (23) |
| ![Structure 6](image6.png) | 1.238 | 260 | Trace | — | 260 (60), 262 (22), 244 (14), 242 (47), 231 (21), 229 (68), 226 (5), 215 (9), 213 (21), 207 (55), 195 (15), 194 (27), 179 (100), 178 (67), 176 (21), 165 (61), 163 (25), 152 (22) |
| ![Structure 7](image7.png) | 1.246 | 260 | Trace | — | 260 (34), 262 (12), 244 (12), 242 (43), 231 (12), 229 (40), 225 (3), 215 (5), 213 (17), 207 (45), 195 (11), 194 (15), 179 (100), 178 (68), 176 (22), 165 (59), 163 (18), 152 (25) |
| ![Structure 8](image8.png) | 1.221 | 260 | Major | — | 260 (82), 262 (57), 227 (16), 225 (51), 190 (61), 189 (100), 187 (34) |
| ![Structure 9](image9.png) | 1.230 | 260 | Minor | — | 260 (100), 262 (68), 227 (24), 225 (70), 190 (32), 189 (64), 187 (21) |
| ![Structure 10](image10.png) | 1.174 | 278 | Minor | — | 278 (37), 230 (19), 244 (7), 243 (12), 242 (18), 229 (13), 227 (13), 226 (15), 225 (33), 208 (31), 207 (15), 191 (18), 190 (19), 189 (28), 179 (100), 178 (71), 176 (24), 165 (35), 163 (16), 152 (13) |
| ![Structure 11](image11.png) | 1.179 | 278 | Trace | — | 278 (43), 230 (31), 245 (35), 244 (26), 242 (36), 226 (16), 191 (19), 190 (18), 189 (27), 179 (34) |
Table 6. (continued)

| Proposed structure | Relative retention time (GC) | Molecular ion, m/z | Amt present | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|------------------------------|--------------------|-------------|-----------------|-----------------|--------------------------|
| COOH(CH₃)          | 1.006                        | 284                | Trace       | Major           |                 | 284 (4), 252 (18), 226 (12), 225 (68), 210 (19), 209 (12), 194 (31), 193 (44), 181 (30), 179 (19), 165 (100) |
| HOOCC(CH₃)         |                              |                    |             |                 |                 |                          |

<sup>a</sup>Reference = 1-methylphenanthrene.

<sup>b</sup>pH = 3.0, [1-methylphenanthrene] = 1.39 × 10⁻⁴, [total chlorine] = 1.0 × 10⁻³, 1 hr required for 7 half-lives.

<sup>c</sup>pH = 8.0, [1-methylphenanthrene] = 1.39 × 10⁻⁴, [total chlorine] = 1.0 × 10⁻³, 23 hr required for 7 half-lives.

<sup>d</sup>Treated with diazomethane prior to analysis by GC/MS.

Table 7. Products of fluoranthene reactions.

| Proposed structure | Relative retention time (HPLC)<sup>a</sup> | Relative retention time (GC)<sup>a</sup> | Molecular ion, m/z | Amt present | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|---------------------------------------------|---------------------------------------------|--------------------|-------------|-----------------|-----------------|--------------------------|
| Cl                 | 1.140                                       | —                                           | 236                | 72%<sup>e</sup> |                 |                 | 236 (100), 238 (29), 201 (32), 200 (50), 199 (13), 198 (15), 100 (18) |
| COOH(CH₃)<sup>d,f</sup> | —                                           | 1.064                                       | 238                | Major       |                 |                 | 238 (29), 208 (18), 207 (75), 180 (69), 179 (48), 152 (28), 151 (72), 150 (56), 75 (100) |
| HCOOH(CH₃)<sup>d,f</sup> | —                                           | 1.247                                       | 294                | Minor       |                 |                 | 294 (19), 236 (20), 235 (100), 220 (40) |

<sup>a</sup>Reference = fluoranthene.

<sup>b</sup>pH = 2.99, [fluoranthene] = 3.32 × 10⁻⁷, [total chlorine] = 3.03 × 10⁻⁴, 242 min required for 4 half-lives.

<sup>c</sup>pH = 8.00, [fluoranthene] = 1.29 × 10⁻⁴, [total chlorine] = 1.82 × 10⁻³, 19 hr required for 4 half-lives.

<sup>d</sup>Relative retention time and mass spectrum are identical to those of an authentic standard.

<sup>e</sup>Determined by HPLC utilizing an authentic compound as a standard. 7% unreacted fluoranthene.

<sup>f</sup>Derivatized with diazomethane prior to GC/MS analysis.

Table 8. Products of pyrene reactions.

| Proposed structure | Relative retention time (GC)<sup>a</sup> | Molecular ion, m/z | Amt present | pH 3<sup>b</sup> | pH 8<sup>c</sup> | m/z (relative abundance) |
|--------------------|---------------------------------------------|--------------------|-------------|-----------------|-----------------|--------------------------|
| d                  | 1.178                                       | 218                | Minor       | 218 (46), 189 (64), 187 (20), 95 (100) |
| OH                 | 1.190                                       | 232                | Major       | 232 (40), 204 (100), 176 (55), 175 (31), 174 (21), 150 (22), 111 (5), 99 (9), 88 (57) |

<sup>a</sup>Reference = pyrene.

<sup>b</sup>pH = 3.0, [pyrene] = 1.39 × 10⁻⁴, [total chlorine] = 1.0 × 10⁻³, 1 hr required for 7 half-lives.

<sup>c</sup>pH = 8.0, [pyrene] = 1.39 × 10⁻⁴, [total chlorine] = 1.0 × 10⁻³, 23 hr required for 7 half-lives.

<sup>d</sup>Treated with diazomethane prior to analysis by GC/MS.
| Proposed structure | Relative retention time (GC) | Molecular ion, m/z | Amt present | pH 3° | pH 8° | m/z (relative abundance) |
|--------------------|-----------------------------|-------------------|-------------|-------|-------|--------------------------|
| [Structure Image]  | 1.196/1.20                  | 232               | Trace       | 232 (100), 204 (29), 176 (75), 174 (18), 150 (15), 88 (30) |
|                    |                             |                   |             | 232 (100), 204 (25), 176 (70), 174 (17), 150 (13), 88 (27) |
| [Structure Image]  | 1.109                       | 236               | Major       | 236 (14), 238 (12), 201 (59), 200 (77), 100 (100) |
| [Structure Image]  | 1.200                       | 248               | Trace       | 248 (13), 204 (77), 176 (62), 175 (56), 174 (22), 150 (16), 88 (100) |
| [Structure Image]  | 1.250                       | 266               | Minor       | 266 (6), 268 (3), 240 (8), 238 (23), 212 (4), 210 (15), 176 (40), 175 (69), 174 (70), 99 (41), 98 (46), 87 (100) |
| [Structure Image]  | 1.172                       | 270               | Major       | 270 (16), 272 (11), 237 (1), 235 (4), 200 (47), 198 (25), 100 (100) |
| [Structure Image]  | 1.217                       | 294               | Major       | 294 (1), 235 (41), 176 (29), 163 (52) |
| [Structure Image]  | 1.234                       | 304               | Trace       | 304 (12), 306 (16), 307 (12), 200 (32), 199 (48), 74 (10) |

*Reference = pyrene.
*pH = 3.0, [pyrene] = 7.1 × 10⁻⁶, [total chlorine] = 1.20 × 10⁻³, 30 min required for 7 half-lives, 8% acetonitrile.
*pH = 8.00, [pyrene] = 6.60 × 10⁻⁶, [total chlorine] = 1.10 × 10⁻³, 90 min required for 4 half-lives, 8% acetonitrile.
*Relative retention time and mass spectrum are identical to those of an authentic standard.
*Mass spectra and relative retention times were identical to data obtained for an authentic mixture of 1,6- and 1,8- pyrenediones.
*Treated with diazomethane prior to GC/MS analysis.
isomers on the basis of prominent M-OH, M-1, M-2 and M-3 peaks in their mass spectra (32). In contrast, 1-chloromethylnaphthalene exhibits a mass spectrum which is nearly identical to that of its ring substituted isomer, 1-chloro-4-methylnaphthalene. Fortunately, a difference in relative gas chromatograph (GC) retention time (1.45 versus 1.38, respectively) allowed the conclusion that the former methyl-substituted halide was not produced in either 1-methyl naphthalene experiment. However, it is not possible to ascertain from the present data whether any of the other chloromethyl derivatives of naphthalene or phenanthrene were formed. A hydroxymethyl group is probably present in only one trace product of methyl naphthalene (Table 1, M+ = 222).

Biological Implications

An assessment of the biological implications of release of these chlorination products into the environment and into drinking water must, at present, depend upon scattered literature reports of various screening tests on individual compounds. These reports indicate that nearly all of the compound types produced in the chlorination reactions of PAH have the potential for causing adverse biological response. However, it is not possible to accurately predict activity of untested products because the nature of the various substituents and their locations on the aromatic ring may drastically affect the biological activity (33).

All of the nonchlorine-containing products of phenanthrene (except diphenic acid) shown in Table 5 have been tested for mutagenic activity by the reversion of histidine-dependent Salmonella typhimurium and the rec assay with Bacillus subtilis (34, 35). The strongest mutagenic activity was observed with phenanthrene-9,10-oxide and 9-phenanthrenol, but this activity was much less than that of the control, benzo[a]pyrene-4,5-oxide. Lack of significant mutagenicity and tumorigenicity of the epoxide and trans-dihydriodiol of phenanthrene was reported by other laboratories (36).

The 1,6- and 1,8-pyrenediones have been reported to be mutagens and enhancing agents to other mutagens (37). Antracquinone shows little or no activity (38), but certain derivatives (e.g., phenols) are quite mutagenic (39). Quinones of benzo(a)pyrene are mutagenic and the Ames assay without microsomal activation (40).

Phenols may be carcinogenic, mutagenic and toxic (18) and may bind to DNA, RNA and proteins (41). Chlorophenols may also exhibit similar activity (42). 2-Naphthol is known to affect the function of renal tubules (43), and 1-naphthol is a reported mutagen (38).

Chlorinated PAHs (e.g., chlorinated dibenzofurans) may be extremely toxic (44, 45). Chloromethyl-(46) and hydroxymethyl-substituted PAHs (47) may also have mutagenic and carcinogenic activity.

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