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Environmental Fate of Five Radiolabeled Coal Conversion By-Products Evaluated in a Laboratory Model Ecosystem

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Anthracene, fluorene, carbazole, dibenzofuran, and dibenzothiophene are five typical by-products of coal conversion which are likely to be environmental pollutants. These were radiolabeled to high specific activity and purity by simple tritium exchange and evaluated for environmental fate in laboratory model ecosystems. Anthracene and fluorene were biologically converted to hydroxy and keto analogs. Carbazole was *N*-methylated and *N*-acetylated. Dibenzothiophene was microsomally oxidized to the sulfoxide and sulfone. Dibenzofuran was relatively inert to biodegradation. The octanol/water partition coefficient for the parent compounds was well correlated with ecological magnification indicating the possibility of predicting environmental behavior from physicochemical parameters.

Introduction

Coal is an extremely complex organic polymer interlaced with inorganic trace impurities. From the structure proposed by Hill and Lyon (*1*), it is evident that fragmentation can embody an astounding variety of polynuclear aromatics, heterocyclic aromatics, phenolics, amines, and heavy metals.

The bituminous coal used in coal hydrogenation in which coal is treated with hydrogen at high pressures and temperatures gives 85% of its weight in liquid and organic products (*2*). In advanced scale laboratory models of coal hydrogenation, many organic products have been isolated either from tars produced by the Synthane process for coal gasification (*3*), in product water (*4*), or in the crude oil produced by the Synthoil process (*5*). For example, more than 80 organic chemicals have been identified by mass spectrometry from synthetic coal tar (*3*).

Relatively large volumes of process water are used in coal conversion processes and the water is contaminated with relatively water soluble organic contaminants. These include phenols, cresols, C_2 and C_3-phenols, acetophenols, dibenzofurans, pyridines, and naphthols (*4*). Thus regardless of the method of hydrogenation, a great variety of organic compounds will be recovered in the crude products of hydrogenation, the finished gas or oil, tars, fly ash, slag, and process water, and may present environmental health hazards to soils, aquatic organisms, vegetations and may transfer to higher trophic levels so as to endanger human health.

Very limited information is available about long-term effects of coal conversion by-products in cooling and drainage waters. Hazdra et al. (*6*) compared the incidence of fish tumors in fish from the polluted Fox River, Illinois, which contained an average of 0.1 ppm of benzanthracene, with unpolluted Lake of the Woods in Ontario, Canada. The Fox River fish contained 4.38% tumors compared with 1.05% in the Canadian fish. Tumors of liver, stomach and skin were particularly common in the Fox River fish.

The toxicity of coal hydrogenation by-products was demonstrated in a pilot plant operation in West Virginia in 1952 (*2, 7*). Despite an aggressive program of industrial hygiene, 51 of the 359 workers assigned to that plant developed skin cancer, an incidence 16–37 times that expected in the normal U. S. population. It was concluded that this was caused by direct contact of the skin with contaminated equipment during normal operation or maintenance and from air-borne materials (*8*). It has

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been reported recently from Los Angeles County that higher lung cancer mortality rates occurred in males living in heavily industrialized areas characterized by elevated levels of benzo[a]pyrene and other polynuclear aromatic compounds of industrial origin in air (*9*).

It is evident that coal hydrogenation will become an important energy source in the future. With hydrogenation plants under design to convert 20,000 tons of coal daily, the environmental toxicology of the organic by-products cannot be overlooked. In this paper we have studied the environmental fate of five coal conversion by-products (*3*) by the laboratory model ecosystem technology (*10*). Anthracene, fluorene, dibenzofuran, dibenzothiophene, and carbazole were radiolabeled with tritium (^3H) to give products of high specific activity and these were evaluated for environmental fate and degradative pathways, and for bioaccumulation over a 33-day period in the water, alga, snail, mosquito larva, and fish of the laboratory model ecosystem. A comparison is made with the environmental fate of the known carcinogen ^{14}C-benzo[a]pyrene studied under identical laboratory model ecosystem conditions.

Materials and Methods

Radiolabeled Compounds

The ^3H-labeled compounds were all prepared by a modification of the method of Hilton and O'Brien (*11*). A 5-ml pear-shaped flask containing 0.33 g of P_2O_5 and fitted with a $CaCl_2$ drying tube was chilled in a Dry Ice and acetone slurry and 0.16 ml of T_2O added by disposable syringe. BF_3 gas was bubbled through the mixture for about 15 min to form an active $T_3PO_4 \cdot BF_3$ complex, to which was added 60 mg of pure compound dissolved in a minimum amount of solvent.

The time allowed for tritium exchange was 6–24 hr. The acid-catalyzed exchange reaction was stopped by adding water and diethyl ether mixture and then stirred overnight. Excess T_2O was removed by extraction and the ^3H-labeled compound was isolated by collection with diethyl ether, dehydration by anhydrous sodium sulfate, and concentration to dryness. The labile tritium in the crude compound was removed by methanol distillation. The purity and specific activity were then determined as summarized in Table 1.

Authentic Model Metabolites

Reagent grade anthracene, anthrone, dibenzofuran, dibenzothiophene, carbazole, fluorene, flurenone, and 9-hydroxyfluorene were all purchased from Aldrich Chemical Co.

Anthranol was prepared by reducing anthrone with sodium borohydride in methanol and then the product was extracted in diethyl ether. The finished product had mp 152°C (lit. 152°C) (*12*).

Dibenzothiophene sulfoxide and sulfone were prepared by oxidizing dibenzothiophene with $HNO_3 \cdot H_2SO_4$ mixture and H_2O_2, respectively. The melting points of the final products are 185°C for dibenzothiophene sulfoxide (lit. 188–188.5°C) (*13*) and 229–230°C for dibenzothiophene sulfone (lit. 229–230°C) (*14*).

Methylation of carbazole with methyl iodide in alcoholic solution yielded the *N*-methylcarbazole, mp 85°C (lit. 87°C) (*15*). Similarly, carbazole reacted with acetic anhydride gave *N*-acetyl carbazole, mp 68–69°C (lit. 68°C) (*16*).

Reagent grade solvents were used for extraction of organisms and water and for TLC developing solvents.

Model Ecosystem Technology

In the terrestrial-aquatic model ecosystem studies (*10, 17*), 5 mg of the pure ^3H-labeled compound was applied from acetone solution to Sorghum leaves in the terrestrial phase of the ecosystem, stimulating the fall out of coal conversion by-products onto the vegetation. The tritiated micropollutant was then monitored throughout the 33 days experimental period. The polluted Sorghum leaves were consumed by the salt marsh caterpillars (*Estigmene acrea*) dispersing the radiolabeled products into the 7 liters of standard reference water (*18*) containing plankton, alga (*Oedogonium cardiacum*), daphnia

Table 1. Summary of physicochemical properties of micropollutants studied in model ecosystem.

Compound	Radiopurity, %	Specific activity, mCi/mM	Water solubility at 25°C, ppm	EM (fish)	Partition coefficient
Anthracene	>99.9	149.95	0.0740	1029	8135
Fluorene	98.6	43.18	4.6380	1400	1345
Carbazole	99.04	68.55	0.9075	125	2560
Dibenzofuran	99.2	25.92	3.1118	947	1527
Dibenzothiophene	>99.78	84.97	0.5291	45	3120

(*Daphnia magna*), and snail (*Physa* sp.). Subsequently, mosquito larvae (*Culex pipiens*) and fish (*Gambusia affinis*) were added to complete the food chain interactions. The entire ecosystem unit in a 10-gal aquarium was kept in a programmed environmental growth chamber for 12 hr daylight cycles of 5000 ft candles light intensity and with constant temperature of 26 ± 1°C.

At the termination of the experiment, the organisms and water samples were collected separately and weighed. The organisms were extracted with acetone and the water extracted with diethyl ether. The total bioaccumulation and the nature of the degradation products was determined by liquid scintillation counting and thin-layer chromatography. The environmental properties of micropollutants were expressed quantitatively as ecological magnification (EM = concentration of parent compound in the organism/concentration of parent compound in the water) and biodegradability index (BI = concentration of polar metabolites/concentration nonpolar metabolites) (*17*).

The unextractable radioactivities (water partitioning metabolites) were assayed by the Schöniger oxygen flask technique (*19*). Quenching was corrected by channels ratio method (*20*). The radiosasay technology, separation, and identification were carried out exactly as previously described (*10, 21*).

Physical Properties

The octanol/water partition coefficients were determined by adding trace quantities of the radiolabeled products to 10 ml of octanol saturated with water and shaking for 1 hr with an equal volume of water saturated with octanol. The immiscible phases were separated by centrifugation and the radioactivity was determined in each phase. Water solubility was determined by shaking saturated solutions of the radiolabeled compounds for 24 hr at 25°C. After filtration and centrifugation the radioactivity was determined in the water (*21*). The values as determined for the five compounds studied are presented in Table 1.

Results and Discussion

Model ecosystem studies provide qualitative and quantitative comparisons of the environmental fate and food chain effects of the polynuclear aromatic and heterocyclic contaminants investigated. The isosteric and isoelectronic relationships of anthracene, fluorene, dibenzothiophene, dibenzofuran, and carbazole afforded interesting comparisons of their biochemical fate in the key organisms of the model ecosystem. The high specific activity of the ^{3}H-radiolabeled compounds permitted detailed examination of their environmental distribution and degradative fate. These observations were quantitatively evaluated and correlated with the physical properties of water solubility and octanol/water partition coefficient.

Model Ecosystem Evaluation

Anthracene: The ^{3}H in the aquatic phase reached a maximum level of 0.2342 ppm after 14 days and decreased to 0.1198 ppm after 33 days. The overall distribution and fate of the ^{3}H-labeled compound is shown in Table 2. The parent compound was substantially stable under the model ecosystem conditions and comprised 41.0% of the total extractable ^{3}H in alga (EM = 670), 22.8% in snail (EM = 2714), 49.5% in mosquito (EM = 631), and 48.3% in fish (EM = 1029). Biologically the major degradative pathway is by microsomal hydroxylation to anthranol (9-hydroxyanthracene, R_f = 0.10) followed by oxidation to anthrone (9-oxo-9,10-dihydroanthracene, R_f = 0.30). Anthranol is much more polar than anthracene (Table 2) and much less bioaccumulative, with EM values of alga, 3; snail, 63; mosquito, 3; and fish, 5. Anthrone is less polar than anthranol and the EM values are

Table 2. Environmental fate of ^{3}H-anthracene in laboratory model ecosystem.

	Anthracene equivalents, ppm				
	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Total extractable ^{3}H	0.09786	0.5715	3.3333	0.4464	0.7456
Unknown I (R_f = 0.73)[a]	—	0.0353	—	—	—
Anthracene (R_f = 0.58)	0.00035	0.2345	0.7610	0.2209	0.3603
Unknown II (R_f = 0.43)	0.00123	0.0239	0.2923	0.0322	0.0100
Anthrone (R_f = 0.30)	0.00017	0.0152	0.1700	0.0003	0.2032
Unknown III (R_f = 0.23)	0.00110	0.0155	0.3147	0.0088	0.0153
Anthranol (R_f = 0.10)	0.00977	0.0312	0.6240	0.0308	0.0547
Polar (R_f = 0.0)	0.03997	0.2159	1.1713	0.1434	0.1021
Unextractable	0.04527	1.8020	2.2910	0.3036	1.3721

[a] TLC with cyclohexane:acetone = 90:10 (v/v).

higher: alga, 89; snail, 1000; mosquito, 60; and fish, 1195.

The relative percentages of these degradation products in the extractable ^3H from the various organisms are compared in Table 3.

The extractable radioactivity accounted for 75.9% of the total radioactivity in alga, 40.7% in snail, 40.4% in mosquito, and 64.7% in fish.

Fluorene: Fluorene differs from anthracene in having a five-membered saturated ring centered between the two six-membered aromatic rings. The radioactivity in the aqueous phase reached a maximum of 0.0569 ppm after 3 days and declined to 0.01224 ppm after 33 days. The overall distribution and fate of the ^3H-labeled compound is shown in Table 4. Fluorene is clearly less environmentally stable than anthracene as shown by the lower relative amounts of parent compound which comprised 5.8% of the total extractable ^3H in alga (EM = 4020), 37.3% in snail (EM = 76,680), 36.3% in mosquito (EM = 3330), and 9.1% in fish (EM = 1400). Biologically, the degradative pathways of fluorene are similar to anthracene, with selective hydroxylation to 9-hydroxyfluorene (R_f = 0.10) which is much more polar and less bioaccumulative with EM values of alga, 306; snail, 447; mosquito, 108; and fish, 14. Further oxidation produced the ketone, 9-fluorenone (R_f = 0.30) which is less polar and had higher EM values: snail, 3060; mosquito, 198; and fish, 380. Relative percentages of these principal degradative products in the extractable ^3H from the various organisms are compared in Table 5.

It is apparent that the fish has a better capacity to detoxify fluorene through microsomal oxidations than the organisms of lower phylogenetic position (*21*).

The unextractable ^3H represents 22.6% of the total radioactivity in alga, 29.7% in snail, 71.1% in mosquito, and 52.7% in fish.

Carbazole: Carbazole is a nitrogen heterocyclic isostere of anthracene and is isoelectronic with dibenzofuran and dibenzothiophene. The ^3H in the aquatic phase reached a maximum of 0.1246 ppm after 14 days and declined to 0.0433 ppm after 33 days. The overall distribution and fate of the ^3H labeled compound is shown in Table 6. The parent compound comprised 10.1% of the total ^3H in alga (EM = 49), 12.3% in snail (EM = 134), 26.8% in mosquito (EM = 112), and 29.3% in fish (EM = 125). Thus carbazole was more readily degraded and less subject to biomagnification than the other compounds studied here. Biologically carbazole was *N*-methylated (R_f = 0.70) and *N*-acetylated (R_f = 0.38), converting to less polar products than the parent compounds. This represents typical environmental behavior for aromatic amines and has been observed with aniline, and diphenylamine in model ecosystem studies (*21*). The relative percentages of these products in the extractable ^3H from the various organisms are compared in Table 7.

Table 3. Relative percentages of degradation products of anthracene.

	Anthracene, %	Anthranol, %	Anthrone, %	Polar, %
Alga	41.0	5.46	2.66	37.77
Snail	22.8	18.72	5.10	35.14
Mosquito	49.5	6.90	23.07	32.12
Fish	48.3	7.34	7.34	13.68

Table 4. Environmental fate of ^3H-fluorene in laboratory model ecosystem.

	Fluorene equivalents, ppm				
	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Total extractable ^3H	0.01768	0.6878	2.0878	0.2971	0.1530
Fluorene (R_f = 0.63)[a]	0.00001	0.0402	0.7668	0.0333	0.0140
Unknown I (R_f = 0.50)	trace	—	0.1922	0.0472	0.0274
Fluorenone (R_f = 0.30)	0.00007	—	0.2142	0.0139	0.0266
Unknown II (R_f = 0.27)	0.00002	0.1171	0.1580	0.0153	0.0411
Unknown IV (R_f = 0.19)	0.00001	0.2147	0.0919	0.0375	0.0065
9-Hydroxyfluorene (R_f = 0.10)	0.00041	0.1256	0.1835	0.0444	0.0061
Polar (R_f = 0.0)	0.00522	0.1902	0.4812	0.1055	0.0313
Unextractable	0.00194	0.2011	0.8803	0.7327	0.1705

[a] TLC with cyclohexane:acetone = 90:10 (v/v).

Table 5. Relative percentages of degradative products of fluorene.

	Fluorene, %	9-Hydroxyfluorene, %	9-Fluorenone, %	Polar, %
Alga	5.8	18.26	—	27.65
Snail	37.3	8.79	10.25	23.05
Mosquito	36.3	14.94	4.68	35.50
Fish	9.1	3.99	17.38	20.46

Table 6. Environmental fate of ^{3}H-carbazole in laboratory model ecosystem.

	Carbazole equivalents, ppm				
	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Total extractable ^{3}H	0.02140	0.2298	0.5757	0.2217	0.2273
N-Methylcarbazole (R_f = 0.70)[a]	—	—	0.0064	0.0437	0.0023
N-Acetylcarbazole (R_f = 0.38)	0.00001	0.0037	0.0442	—	0.0026
Carbazole (R_f = 0.27)	0.00053	0.0231	0.0709	0.0593	0.0665
Unknown III (R_f = 0.18)	—	—	0.0279	—	0.0004
Unknown IV (R_f = 0.11)	0.00002	—	0.0197	0.0071	0.0012
Unknown V (R_f = 0.07)	0.00003	0.2006	0.1063	0.0422	0.0053
Polar (R_f = 0.0)	0.00453	0.0024	0.3003	0.0694	0.1490
Unextractable	0.01628	0.1805	1.4977	0.9950	0.2666

[a] TLC with cyclohexane:acetone = 90:10 (v/v).

Table 7. Relative percentages of products from carbazole.

	Carbazole, %	*N*-Methyl-carbazole, %	*N*-Acetyl-carbazole, %	Polar, %
Alga	10.1	—	1.61	1.04
Snail	12.3	1.11	7.68	52.16
Mosquito	26.8	19.71	—	31.30
Fish	29.3	1.01	1.14	55.55

Other more polar degradation products of carbazole were found (R_f = 0.18, R_f = 0.11, and R_f = 0.07). These presumably represent ring-hydroxylated compounds but were not identified. Unextractable ^{3}H was relatively high in all the organisms and comprised 43.9% of the total ^{3}H in alga: 72.7% in snail, 81.8% in mosquito, and 53.9% in fish.

Dibenzofuran: Dibenzofuran is a heterocyclic oxygen compound isosteric with carbazole and dibenzothiophene. The ^{3}H in the aqueous phase reached a maximum level of 0.0352 ppm after 2 days and declined to 0.0142 ppm after 33 days. The overall distribution and fate of the ^{3}H labeled compound is shown in Table 8. The parent compound represented 9.3% of the total extractable ^{3}H in alga (EM = 82), 30.9% in snail (EM = 2858), 56.3% in mosquito (EM = 2094), and 48.4% in fish (EM = 947). All of the degradation products (unknowns I-IV) were substantially more polar than dibenzofuran and presumably represent ring hydroxylated compounds. The polar ^{3}H represented 68.6% of the total extractable radioactivity in alga, 41.0% in snail, 25.0% in mosquito, and 13.7% in fish. The unextractable ^{3}H was 30.3% of the total radioactivity in alga, 37.5% in snail, 27.1% in mosquito, and 29.7% in fish.

Dibenzothiophene: Dibenzothiophene is a heterocyclic sulfur isostere of dibenzofuran and carbazole. The ^{3}H in the aqueous phase reached a maximum level of 0.0905 ppm after 5 days and declined to 0.0218 ppm after 33 days. The overall distribution and fate of the ^{3}H labeled compound is shown in Table 9. The parent compound represented 39.3% of the total extractable ^{3}H in alga (EM = 138), 33.2% in snail (EM = 1505), 24.9% in mosquito (EM = 356), and 9.7% in fish (EM = 45). The principal degradative pathway in the model ecosystem environment was the microsomal oxidation to dibenzothiophene sulfoxide (R_f = 0.17) followed by further oxidation to dibenzothiophene sulfone (R_f = 0.47). The sulfoxide is much more polar than the parent compound, and this represents a mechanism for elimination of the compound from animal bodies, especially in higher forms such as fish (*22*). The relative percentages of these products in the extractable ^{3}H from the various organisms are compared in Table 10. The microsomal oxidative system is most highly developed in the fish, which was the only organism containing appreciable amounts of sulfone.

The effect of the greater polarity of dibenzothiophene sulfoxide is shown by the reduced EM values compared to the parent compound: alga, 0; snail, 257; mosquito, 69; and fish, 0. Similarly the EM value for the sulfone in the fish was 0. The unknown degradation products (R_f = 0.36, 0.26, and 0.09) are presumably ring-hydroxylation products. The unextractable radioactivity represented 88.6% of the total radioactivity in alga, 19.9% in snail, 47.9% in mosquito, and 61.9% in fish. The overall environmental behavior of dibenzothiophene was very similar to that observed in comparable studies with ^{14}C-phenothiazine (*23*).

Comparison with Benzo[a]pyrene

Benzo[a]pyrene, one of the most active carcinogens found in coal conversion products (*3*), has been studied under identical model ecosystem conditions (*24*). Benzo[a]pyrene is very insoluble in water (0.172 ppb) and has a high octanol/H_2O partition of 11,140. Thus, it can be predicted that ben-

Table 8. Environmental fate of ^{3}H-dibenzofuran in laboratory model ecosystem.

	Dibenzofuran equivalents, ppm				
	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Total extractable ^{3}H	0.00917	0.0625	0.6459	0.2595	0.1371
Dibenzofuran (R_f = 0.63)[a]	0.00007	0.0058	0.2001	0.1466	0.0663
Unknown I (R_f = 0.51)	0.00005	—	0.0509	0.0408	0.0343
Unknown II (R_f = 0.44)	0.00002	0.0058	0.0386	—	0.0144
Unknown III (R_f = 0.20)	0.00004	0.0080	0.0913	0.0072	0.0033
Unknown IV (R_f = 0.10)	0.00021	—	—	—	—
Polar (R_f = 0.0)	0.00146	0.0429	0.2650	0.0649	0.0188
Unextractable	0.00732	0.0272	0.3880	0.0969	0.0580

[a] TLC with cyclohexane:acetone = 90:10 (v/v).

Table 9. Environmental fate of ^{3}H-dibenzothiophene in laboratory model ecosystem.

	Dibenzothiophene equivalents, ppm				
	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Total extractable ^{3}H	0.02205	0.0211	2.7185	0.8592	0.0277
Dibenzothiophene (R_f = 0.71)[a]	0.00006	0.0083	0.0903	0.2140	0.0027
DBT-SO_2 (R_f = 0.47)	0.00396	—	—	—	0.0038
Unknown I (R_f = 0.36)	0.00006	—	—	—	—
Unknown II (R_f = 0.26)	0.00017	0.0049	0.0856	0.0245	0.0043
DBT-SO (R_f = 0.17)	0.00159	0.0026	0.4086	0.1101	0.0010
Unknown III (R_f = 0.09)	0.00143	0.0014	0.3045	0.0688	0.0125
Polar (R_f = 0.0)	0.00637	0.0039	1.8295	0.4418	0.0034
Unextractable	0.00841	0.1636	0.6751	0.7929	0.0449

[a] TLC with benzene:acetone = 90:10 (v/v).

Table 10. Relative percentages of products from dibenzothiophene.

	Dibenzothiophene, %	Dibenzothiophene sulfoxide, %	Dibenzothiophene sulfone, %	Polar, %
Alga	39.3	12.32	—	18.48
Snail	33.2	15.03	—	67.30
Mosquito	24.9	12.81	—	51.42
Fish	9.7	3.61	13.71	12.27

zo[a]pyrene can be bioaccumulated in aquatic organisms. However, this polynuclear aromatic has a number of sites for epoxidation and hydroxylation (*25*) and these lead to ready conjugation and excretion. Benzo[a]pyrene is also highly photodegradable. Thus the initial uptake and bioconcentration shown in 3-day studies is greatly reduced over the 33-day model ecosystem study. However, the extreme carcinogenic and mutagenic potential of this compound make even the ppb quantities found in the model ecosystem organisms (*24*) highly suspect. Tissue levels stored in organisms are very sensitive to the presence of microsomal oxidase inhibitors such as piperonyl butoxide and this compound has been shown to act as a cocarcinogen (*26*).

Bioaccumulation and Partition Coefficients

The partitioning of organic chemicals between lipid and water is an important determinant of biological activity of pharmaceuticals and pesticides and an indicator of *in vivo* pathways of degradative metabolism. Recently, good correlation has been observed between octanol/water partition coefficients and bioaccumulation of organic compounds in the fish *Salmo gairdneri* (*27, 28*) and *Gambusia affinis* (*21*).

The environmental behavior of the five coal conversion by-products studied here can be predicted by this established relationship as shown in Figure 1. Anthracene, dibenzofuran, and fluorene fit this

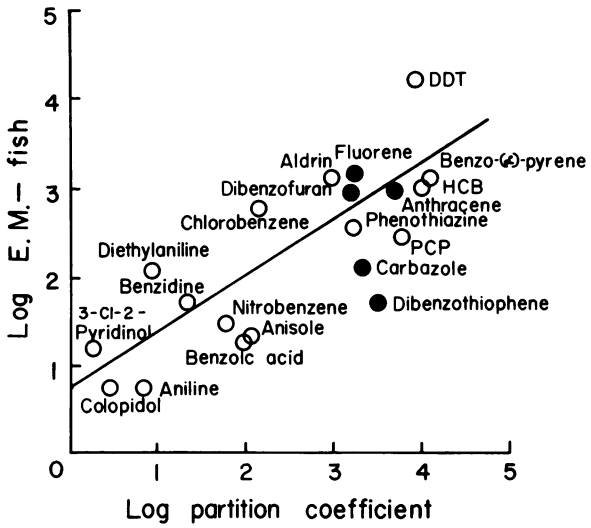

FIGURE 1. Relationship of log partition coefficient and ecological mangification of a variety of organic compounds: (○) values from Lu and Metcalf (*21*) and Coats et al. (*23*); (●) present work.

relationship well. The behavior of carbazole is explained by the metabolic conversion of carbazole to *N*-methyl and *N*-acetyl derivatives and of dibenzothiophene to sulfoxide and sulfone. These biological conversions produce appreciable changes in the octanol/water partition ratios, which are reflected in the degrees of biomagnification.

Conclusions

Anthracene is very insoluble in water with a moderately high octanol/water partition coefficient as shown in Table 1, and tends to be bioaccumulated. However, hydroxylation of the aromatic rings changes the polarity of the molecule, and thus the phenols produced are eliminated more easily. In contrast, the further oxidation product, anthrone, has the same degree of persistency as the parent compound. The balance of the formation of anthranol and anthrone in the living organisms will determine the magnitude of bioaccumulation.

Dibenzofuran, dibenzothiophene, and carbazole with heterocyclic structures are relatively more water soluble than anthracene (Table 1). Carbazole has a pyrrole ring subject to methylation or acetylation as the important metabolic pathways. Dibenzothiophene is subject to oxidation to sulfoxide and sulfone metabolites which further increase the polarity. Dibenzofuran does not possess a degradophore and shows substantial accumulation.

Fluorene with a saturated carbon atom is somewhat anomalous and is clearly more water soluble than the aromatic anthracene (Table 1). Fluorene has similar metabolic pathways to anthracene for the formation of alcohol and ketone analogs and shows high level of magnification.

Data obtained from model ecosystem studies and physical properties determined experimentally (Table 1) clearly indicate a satisfactory relationship between octanol/water partition coefficient and ecological magnification in the fish as shown in Figure 1. The five tritiated compounds under study here and benzo[a]pyrene fit well into this relationship as previously established for simple benzene derivatives and organic intermediates (*21*) and pesticides (*29*). Thus the techniques used here provide a relatively simple inexpensive, and useful way to evaluate the environmental fate of the large variety of organic wastes produced in coal conversion.

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