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Residues of Pesticides and Other
Contaminants in the Total Environment

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Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems

By
R. C. Sims* and M. R. Overcash**

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I. Introduction

a) Chemical structure, properties, production, sources, and historical perspectives

Polycyclic aromatic hydrocarbons (PAH) consist of three or more fused benzene rings in linear, angular, or cluster arrangements. Substitution of carbon in the benzene ring with nitrogen, sulfur, oxygen, or other elements creates heterocyclic aromatic compounds (Blumer 1976). Excluding diphenyl types there are some 70 possible isomers of 4-6 fused rings. Additionally these isomers may be substituted by a variety of substituents (Erskine and Whitehead 1975). The aromatic hydrocarbons and heterocycles, unsubstituted and substituted, are referred to alternatively as polynuclear aromatics (PNAs), polycyclic aromatic compounds (PCAs), and polycyclic organic matter (POM) (NAS 1972, U.S. EPA 1975 b).

PNAs are geochemically stable compounds which tend to be preserved in sediments and sedimentary rocks. Relative stability among PNAs is indicated by ring arrangement. Ring patterns and relative stabilities are indicated in Table I (Blumer 1976).

Structures and physical-chemical properties for several PNAs are given in Table II. The PNAs described are those listed in the U.S. Environmental Protection Agency's Consent Decree Priority Pollutant list (U.S. EPA 1976).

Production of PNAs is due to both natural and man-made processes. Table III summarizes the various sources for the production of PNAs in the environment. Table IV presents quantitative information concerning the emissions to the environment of the most studied PNA, benz(a)pyrene (B(a)P). It is apparent from Tables III and IV that anthropogenic sources are the most significant sources for PNA production and introduction into the environment.

It has been further determined (Blumer and Youngblood 1975, Giger and Blumer 1974) that the temperatures associated with pyrolysis of organic compounds determine the types of aromatic compounds that are produced. Table V summarizes the effect of temperature on extent of alkyl substitution.

With petroleum, although the PNA level is relatively low (0.4 to 1.4 ppm B(a)P), catalytic cracking processes are known to increase the PNAs which will

Table I. *Ring arrangement and relative stability* (Blumer 1976).

Ring Arrangement	linear	cluster	angular
Description	all rings in line	at least one ring surrounded on three sides	rings in steps
Stability	least	intermediate	most
Examples	anthracene tetracene	pyrene benzopyrene	phenanthrene chrysene

Table II. *Stru*

PNA	S
Naphthalene	
Acenaphthene	
Acenaphthylene	
Anthracene	
Phenanthrene	
Fluorene	
Fluoranthene	
Benz(a)anthracene	
Chrysene	
Pyrene	
Benz(a)pyrene	
Benzo(b)fluoranthene	
Benzo(k)fluoranthene	
Dibenz(a,h)-anthracene	
Benzo(ghi)perylene	
Indeno(1,2,3-cd)-pyrene	

[a] mp = melting point.
[b] bp = boiling point.
[c] log K_p = logarithm o

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Table II. *Structures and physical-chemical properties of PNAs.*

PNA	Structure (no. of rings)	mp[a] °C	bp[b] °C	Aqueous solubility (mg/L)	log K_p[c]	Vapor pressure (torr at 20°C)
Naphthalene	2	80	218	30	3.37	4.92×10^{-2}
Acenaphthene	3	96	279	3.47	4.33	2.0×10^{-2}
Acenaphthylene	3	92	265	3.93	4.07	2.9×10^{-2}
Anthracene	3	216	340	0.07	4.45	1.96×10^{-4}
Phenanthrene	3	101	340	1.29	4.46	6.80×10^{-4}
Fluorene	3	116	293	1.98	4.18	1.3×10^{-2}
Fluoranthene	4	111	–	0.26	5.33	6.0×10^{-6}
Benz(a)anthracene	4	158	400	0.014	5.61	5.0×10^{-9}
Chrysene	4	255	–	0.002	5.61	6.3×10^{-7}
Pyrene	4	149	360	0.14	5.32	6.85×10^{-7}
Benz(a)pyrene	5	179	496	0.0038	6.04	5.0×10^{-7}
Benzo(b)fluoranthene	5	167	–	0.0012	6.57	5.0×10^{-7}
Benzo(k)fluoranthene	5	217	480	0.00055	6.84	5.0×10^{-7}
Dibenz(a,h)-anthracene	5	262	–	0.0005	5.97	1.0×10^{-10}
Benzo(ghi)perylene	6	222	–	0.00026	7.23	1.0×10^{-10}
Indeno(1,2,3-cd)-pyrene	6	163	–	0.062	7.66	1.0×10^{-10}

[a] mp = melting point.
[b] bp = boiling point.
[c] log K_p = logarithm of the octanol:water partition coefficient (Vesar 1979).

concentrate in residual products (Horton *et al.* 1963). Automotive lubricant oil will typically demonstrate an increase in B(a)P from 0.03 ppm to 5.8 ppm after 1,400 miles (Graf and Winter 1968). Thus PNA levels in products and in fuel oils depend upon crude oil source and upon the processing involved.

Organic geochemical reactions also produce PNAs. The apparent transformation of α-pinene to *p*-cymene (Skrigan 1951) and of abietic acid to retene in fossil pine stumps (Skrigan 1965) indicates that dehydrogenation of aliphatic compounds to aromatic compounds is an important geochemical reaction. Laboratory dehydrogenation of lanosterol with selenium yields 1,2,8-trimethylphenanthrene indicating that diagenesis of plant sterols would have given rise to this hydrocarbon (Mair and Martinez-Pico 1962).

Anthropogenic combustion of fossil fuels including wood, coal, and oil is believed to be the major source of PNAs identified in sediments in Massachusetts (Hites *et al.* 1977). Increased use of U.S. coal deposits by converting this resource to synthetic oil and gas products, termed synfuels, will greatly increase the production of PNAs and their possible introduction into the multimedia environment (Jackson 1979, Braunstein *et al.* 1977).

Table III. *Production of PNAs in the environment.*

Anthropogenic		Non-anthropogenic	
I. Industry	**Reference**	**I. Geochemistry**	**Reference**
fossil fuels (gasification, liquefaction)	Hites *et al.* (1977)	coal	Diehl *et al.* (1967)
	Jackson (1979)		Hayatsu *et al.* (1975)
	Braunstein *et al.* (1977)		Braunstein *et al.* (1977)
heating and power	NAS (1972)	curtisite	Geissman *et al.* (1967)
	Suess (1976)	sedimentary rocks	Hodgson *et al.* (1968)
coke production	Suess (1976)	minerals associated with mercury ores	Blumer (1975)
	Griest & Herbes (1978)		
catalytic cracking	Ershova (1971)	volcanic activity	Suess (1976)
	Suess (1976)		Il'Nitskii *et al.* (1977)
	Tye *et al.* (1966)	minerals	Murdoch & Geissman (1967)
carbon black	NAS (1972)		
asphalt hot road mix processes	NAS (1972)	geochemical reactions of biogenic molecules	Eglinton & Murphy (1968)
	Sawicki *et al.* (1965)		
internal combustion engine	Colucci & Begeman (1971)		
	NAS (1972)		
coal tar pitch	NAS (1972)		
wastewater	Il'Nitskii (1966)		
food preparation	Bailey & Dungal (1958)		
	Panalaks (1976)		
II. Open burning		**II. Biochemical synthesis**	
refuse	Hangebrauck *et al.* (1964)	plants	Borneff *et al.* (1968 a)
tires	Hangebrauck *et al.* (1964)		Borneff *et al.* (1968 b)
grass, leaves	Junk & Ford (1980)		Grimmer & Duvel (1970)
	Youngblood & Blumer (1975)	anaerobic bacteria	Hase & Hites (1976)
forest and agriculture	Suess (1976)	bacteria	Mallet *et al.* (1967)
	Ryan & McMahon (1976)		Niaussat *et al.* (1970)
municipal incinerators	Davies *et al.* (1976)		

Table IV. *Estimated Benzo(a)pyrene emissions* (Suess 1976).

Source	B(a)P (tons/year) U.S.A.	Worldwide (excluding U.S.A.)	Worldwide
Heating and power generation using			
coal	431	1945	2376
oil	2	3	5
gas	2	1	3
wood	40	180	220
subtotal	475	2129	2604
Industrial processes			
coke production	192	841	1033
catalytic cracking	6	6	12
subtotal	198	847	1045
Refuse and open burning			
enclosed incineration			
commercial and industrial	23	46	69
other	11	22	33
open burning			
coal refuse fires	340	340	680
forest and agriculture	140	280	420
other	74	74	148
subtotal	588	762	1350
Vehicles			
trucks and buses	12	17	29
automobiles	10	6	16
subtotal	22	23	45
TOTAL	1283	3761	5044

Table V. *Effect of temperature on alkyl substitution of PNAs.*

Temperature	Source	Alkyl substitution
High (2,000°C)	internal combustion engine	few alkyl substituents
Intermediate (400°-800°C)	wood fires	abundance of alkyl side chains increases with decreasing temperature
Low (100°-150°C)	petroleum	numerous alkyl substituents

It is also recognized that a major part of PNAs in air must sediment on terrestrial systems by rain and snow (NAS 1972, Shabad 1975). Also PNAs in wastewater and aquatic systems move into sediments due to their low solubilities in aqueous systems (refer to Table II for log K_p values) (Lee *et al.* 1978, Griest and Herbes 1978). Thus soil and sediment act as ultimate sinks for PNAs in the multimedia environment.

A natural balance between the production and the degradation of PNAs existed prior to the twentieth century. PNA synthesis by endogenous factors including microorganisms and volcanic activity and by exogenous factors including man-made high temperature pyrolytic reactions and open burning were balanced by PNA destruction via photodegradation and microbial transformation. However, with increased industrial development and with increased emphasis on the utilization of fossil fuels as an alternative energy source, the natural balance is greatly disturbed with the result that the production of PNA and introduction into the environment greatly exceeds present processes for removal of PNAs (Suess 1976, Jackson 1979, Hites *et al.* 1977).

b) Distribution

PNAs are found distributed throughout the multimedia environment. Table VI summarizes the occurrence and concentrations of individual PNAs in soils and sediments worldwide. It is obvious from the table that PNA levels in soils and sediments are higher in closer proximity to anthropogenic activity (industry and residential areas). Soil samples taken in agricultural areas, far from cities, industrial plants, and highways contain B(a)P levels not more than 5 to 10 μg/kg dry weight. This level is the normal background level in U.S.S.R. soils and is suggested as the background of B(a)P in the global terrestrial environment (Shabad 1975).

Non-anthropogenic distribution of PNAs is primarily associated with fossil fuels and minerals resulting from geochemical reactions within the earth's crust. Coal is predominantly an aromatic material (Hayatsu *et al.* 1975). Table VII lists aromatic components and heterocycles found in bituminous coal (Wiser 1973). Wiser (1973) sugggests that up to 75% of the carbon present in bituminous coal is aromatic, with a multitude of five- and six-membered rings.

PNA minerals occur in association with mercury ores, bituminous substances, and hot springs gases worldwide. Curtisite, a greenish-yellow, fluorescent soft mineral, occurring at surface vents of the hot springs at Skaggs Springs, Sonoma County, California, was first described by Wright and Allen and a related mineral idrialite was reported from Ordejov, Moldavia, Czechoslovakia, by Tucek and Kourimsky (Blumer and Youngblood 1975). The mineral pendletonite is nearly pure coronene and was reported from the New Idria Mine, San Benito County, California (Murdoch and Geissman 1967). Table VIII is a summary of these PNA-mineral associations (Blumer 1975). The alkylation patterns in the homologous series of idrialite and curtisite resemble those from soils, marine sediments, and wood tars. Thus intermediate pyrolysis temperatures are indicated, which

permit the survival of intermediate alkylation (Blumer 1975, Blumer and Youngblood 1975).

The ubiquitous distribution of PNAs in terrestrial systems may also be related to plant-lignin decomposition under coalification conditions. Lignin decomposition products include phenols, quinones, and polymerization products. Under the conditions of coalification, the formation of polymerization products derived from quinonoid substances may occur. This leads to a higher degree of aromatization (Flaig 1965).

In addition to the in-situ formation of PNAs in geochemical reactions and local production of PNAs from anthropogenic sources, two transportation modes are believed responsible for additional dispersion world-wide: (1) resuspension and transport of contaminated sediments found near urban areas; and (2) long-range airborne transport of urban air particulates. Data on PNA concentration gradients in Massachusetts Bay sediment and Gulf of Maine sediment (Table VI) support the concept of sediment transport; data on soils and sediments remote from human activity support the concept of airborne transport (Windsor and Hites 1979).

c) Toxicity

PNAs, many of which are carcinogenic, constitute one of the more significant groups of chemicals in the environment which might be of concern. Pott's observations in 1775 that scrotal cancer in chimney sweeps was the result of a component of soot was the first suggestion that cancer could be caused by environmental agents. A century later Yamagiwa and Ichikawa demonstrated the systematic induction of skin cancer in rabbits with coal tar extracts. Shale tars, used to reduce wind erosion of soil in the U.S.S.R., induced papillomas and carcinomas in mice (Shabad 1975). The search for the active substance in coal-related material resulted in the isolation and identification of benz(a)pyrene by British scientists 120 yrs after Pott's observations

At the present time there is a dearth of information concerning acute toxicity of PNAs. Acute toxicities to fish of 1-, 2-, and 3-ring aromatic hydrocarbons indicate a general 10-fold increase in toxicity, measured as 48 hr lethal concentration at which one-half the population of animals died, *i.e.*, LC_{50} (mg/L), per 40 to 50 unit increase in molecular weight. Data for benzene, toluene, and xylene indicate that methylation may decrease toxicity. No toxicity data are available for 4- and 5-ring PNAs. The idea that solubility may play a critical role in toxicity to fish is suggested by the observation that anthracene, which is 20 times less soluble than phenanthrene, is not toxic to fish even in supersaturated solutions (McKee and Wolf 1963).

While acute effects of heterocyclic analogs of aromatic hydrocarbons have not been studied in detail, thiophene is known to be 33% more toxic to sunfish than is benzene (Jones 1964) and thiophene and 2-methylthiophene are more toxic to mammals than are the benzene analogs (Herbes *et al.* 1976).

Table VI. *Distribution of PNAs in soils and sediments.*

PNA	Site		Concentration	Comment	Reference
	Type	Location	(μg/kg, dry wt)		
Benz(a)pyrene	soil	Moscow, USSR	8010	petroleum refinery	Shabad *et al.* (1969)
Benz(a)pyrene	estuarine sediment	Bay of Naples Naples, Italy	3030	Bagnoli, black mud	Bourcart & Mallet (1965)
Benz(a)pyrene	marine sediment	North Sea, off French Coast	0-1670	bottom mud	Mallet *et al.* (1963)
Benz(a)pyrene	estuarine sediment	Bay of Naples Naples, Italy	958	Torre del Greco, black mud	Bourcart & Mallet (1965)
Benz(a)pyrene	soil	Moscow, USSR	890	old area of city	Shabad *et al.* (1969)
Benz(a)pyrene	estuarine sediment	Bay of Naples Naples, Italy	562	Ischia, black mud	Bourcart & Mallet (1965)
Benz(a)pyrene	estuarine sediment	Bay of Naples Naples, Italy	533	San Biovanni, black mud	Bourcart & Mallet (1965)
Benz(a)pyrene	estuarine sediment	Buzzards Bay Mass.	370	0.5 mile from shore	Giger & Blumer (1974)
Benz(a)pyrene	soil	Moscow, USSR	270	suburban residential	Shabad *et al.* (1969)
Benz(a)pyrene	agricultural soil	France	260	Creuse (soil surface)	Binet & Mallet (1963)
Benz(a)pyrene	estuarine sediment	Buzzards Bay Mass.	75	1.3 mile from shore	Giger & Blumer (1974)
Benz(a)pyrene	agricultural soil	Ceske Budejovice Czechoslovakia	42.1	clay	Kolar *et al.* (1975)
Benz(a)pyrene	agricultural soil	Ceske Budejovice Czechoslovakia	37.7	clayey soil	Kolar *et al.* (1975)
Benz(a)pyrene	soil	Moscow, USSR	18	suburban forest	Shabad *et al.* (1969)
Benz(a)pyrene	agricultural soil	Kremze, Czechoslovakia	16.5	sandy clay	Kolar *et al.* (1975)

Benz(a)pyrene	estuarine sediment	Buzzards Bay Mass.	75	1.3 mile from shore	Giger & Blumer (1974)
Benz(a)pyrene	agricultural soil	Ceske Budejovice Czechoslovakia	42.1	clay	Kolar *et al.* (1975)
Benz(a)pyrene	agricultural soil	Ceske Budejovice Czechoslovakia	37.7	clayey soil	Kolar *et al.* (1975)
Benz(a)pyrene	soil	Moscow, USSR	18	suburban forest	Shabad *et al.* (1969)
Benz(a)pyrene	agricultural soil	Kremze, Czechoslovakia	16.5	sandy clay	Kolar *et al.* (1975)
Benz(a)pyrene	agricultural soil	Kremze, Czechoslovakia	8.3	argillaceous sand	Kolar *et al.* (1975)
Benz(a)pyrene	forest soil	near Lake Constance, Germany	1.5-2.5	spruce, mixed, beech woods	Harrison *et al.* (1975)
Benz(a)pyrene	forest soil	Bodensee area, Germany	1.5-2.5	fir, beech, mixed conifer	Borneff & Kunte (1963)
Benz(a)pyrene	estuarine sediment	Bay of Naples Naples, Italy	1.4	Capri, sand	Bourcart & Mallet (1965)
Benz(a)pyrene	garden soil	South Bohemia	0.010-0.04	rural area	Hites *et al.* (1977)
Pyrene	estuarine sediment	Buzzards Bay Mass.	960	0.5 mile from shore	Giger & Blumer (1974)
Pyrene	estuarine sediment	Buzzards Bay Mass.	100	1.3 mile from shore	Giger & Blumer (1974)
Pyrene	forest soil	Bodensee area Germany	10-15	pine, beech, mixed conifer	Borneff & Kunte (1963)
Benz(a)anthracene	estuarine sediment	Buzzards Bay Mass.	330	0.5 mile from shore	Giger & Blumer (1974)
Benz(a)anthracene	estuarine sediment	Buzzards Bay Mass.	41	1.3 mile from shore	Giger & Blumer (1974)
Benz(a)anthracene	forest soil	Bodensee area, Germany	10	pine, beech, mixed conifer	Borneff & Kunte (1963)
Benzo(ghi)perylene	estuarine sediment	Buzzards Bay Mass.	280	0.5 mile from shore	Giger & Blumer (1974)
Benzo(ghi)perylene	estuarine sediment	Buzzards Bay Mass.	66	1.3 mile from shore	Giger & Blumer (1974)
Benzo(ghi)perylene	forest soil	near Lake Constance, Germany	10-20	spruce, beech, mixed woods	Harrison *et al.* (1975)
Perylene	estuarine sediment	Buzzards Bay Mass.	94	0.5 mile from shore	Giger & Blumer (1974)
Perylene	estuarine sediment	Buzzards Bay Mass.	26	1.3 mile from shore	Giger & Blumer (1974)

Table VI (*continued*)

PNA	Site: Type	Site: Location	Concentration (μg/kg, dry wt)	Comment	Reference
Perylene	marine sediment	Gulf of Mexico	0.1-12		Bartle *et al.* (1976)
Benz(e)pyrene	estuarine sediment	Buzzards Bay Mass.	310	0.5 mile from shore	Giger & Blumer (1974)
Benz(e)pyrene	estuarine sediment	Buzzards Bay Mass.	59	1.3 mile from shore	Giger & Blumer (1974)
Chrysene	estuarine sediment	Buzzards Bay Mass.	240	0.5 mile from shore	Giger & Blumer (1974)
Chrysene	estuarine sediment	Buzzards Bay Mass.	40	1.3 mile from shore	Giger & Blumer (1974)
Anthanthrene	estuarine sediment	Buzzards Bay Mass.	34	0.5 mile from shore	Giger & Blumer (1974)
Anthanthrene	estuarine sediment	Buzzards Bay Mass.	7	1.3 mile from shore	Giger & Blumer (1974)
Coronene	estuarine sediment	Buzzards Bay Mass.	20	0.5 mile from shore	Giger & Blumer (1974)
Coronene	estuarine sediment	Buzzards Bay Mass.	5	1.3 mile from shore	Giger & Blumer (1974)
Anthracene	estuarine sediment	Buzzards Bay Mass.	170	0.5 mile from shore	Giger & Blumer (1974)
Fluoranthene	forest soil	Bodensee area Germany	25-40	pine, beech, mixed conifer	Borneff & Kunte (1963)
Phenanthrene	estuarine sediment	Buzzards Bay Mass.	33	1.3 mile from shore	Giger & Blumer (1974)
Benzo(b)fluoranthene	forest soil	Bodensee area Germany	20-30	pine, beech, mixed conifer	Borneff & Kunte (1963)
1,12-Benzperylene	forest soil	Bodensee area Germany	10-20	pine, beech, mixed conifer	Borneff & Kunte (1963)
Benzo(k)fluoranthene	forest soil	Bodensee area Germany	10-15	pine, beech, mixed conifer	Borneff & Kunte (1963)
Indeno(1,2,3-cd)-pyrene	forest soil	Bodensee area Germany	10-15	pine, beech, mixed conifer	Borneff & Kunte (1963)

Table VII. *Aromatic components and heterocycles in bituminous coal.*

I. Hydrocarbons	III. Nitrogen heterocyclics
benzene	pyridine
naphthalene	quinoline
phenanthrene	carbazole
fluoranthene	
II. Sulfur heterocyclics	**IV. Oxygen heterocyclics**
benzothiophene	benzofuran
dibenzothiophene	dibenzofuran

Subacute effects of PNAs, including carcinogenicity and mutagenicity, are of major concern and have been studied more intensively. Fish from industrially contaminated rivers have been shown to develop four times more tumors than fish in unpolluted water (Brown *et al.* 1973). Lee *et al.* (1978) demonstrated a rapid bioaccumulation of PNAs including naphthalene, anthracene, fluoranthene, benz(a)anthracene, and benz(a)pyrene by oysters. The rate of excretion of these PNAs after transfer to uncontaminated water was inversely proportional to molecular size. Calculated half-lives assuming exponential discharge from the oysters ranged from 2 days for naphthalene to 18 days for B(a)P. The ability of PNAs to bioaccumulate in living organisms was also demonstrated by Southworth *et al.* (1978). PNAs were concentrated from a high of 10,000-fold for benz(a)anthracene to a low of 100-fold for naphthalene with *Daphnia pulex* test organisms.

PNAs can be taken into the body by inhalation, skin contact, or ingestion, although they are poorly absorbed from the gastrointestinal tract. The main routes of elimination of both PNAs and their metabolites include the hepatobiliary system and the GI tract (Braunstein *et al.* 1977).

Research into the biochemical mechanisms of action of chemical carcinogens is the result of development of sensitive bioassays and analytical techniques for analyses of the highly reactive and transient intermediates formed during the metabolism of PNAs. Animal studies indicate that PNAs are metabolized by liver

Table VIII. *PNA-mineral associations in the earth's crust* (Blumer 1975).

Mineral	PNAs	Mineral	PNAs
Curtisite	benzofluorene	Idrialite	tribenzofluorene
	chrysene		benzopicene
	dibenzofluorene		pentabenzothiophene
	tetrabenzothiophene		tetrabenzofluorene
	coronene		dibenzopicene
	anthanthrene		picene
	picene		

mixed function oxidases to epoxides, dihydrodiols, phenols, and quinones. These reactions represent an intoxication of the parent PNA as the metabolites have been identified as the mutagenic, carcinogenic, and teratogenic agents. Electrophilic metabolites of PNAs (epoxides) have been demonstrated to bind to genetic material including DNA and RNA which represent the basis of tumor initiation (Braunstein 1977, Hodgson and Guthrie 1980, Wright 1980, Bigger *et al.* 1980, Simmon and Baden 1980).

Metabolic formation of bay region diol epoxides represents an important pathway by which PNAs are activated to carcinogens. Such metabolic activation proceeds via initial formation of the dihydrodiol with the bay region double bond, followed by subsequent oxidation of the dihydrodiol to the bay region diol epoxide. Metabolic activation of B(a)P to bay region diol epoxides is illustrated in the following scheme (Thakker *et al.* 1979) (Fig. 1).

Liver microsomal enzymes of trout fish were shown to activate B(a)P, 2-aminofluorene, and 2-acetylaminofluorene to compounds which are potent frameshift mutagens in the Ames *Salmonella typhimurium*/mammalian microsome assay (Ahokas *et al.* 1976).

The effects of PNAs on terrestrial and aquatic organisms is summarized in Table IX. While Hass and Applegate (1975) demonstrate a structure-specific response of microorganisms to PNAs, Calder and Lader (1976) demonstrated that PNAs inhibited the growth of bacteria in a manner which was dose-related and a function of water solubility. Saturated solutions of B(a)P and naphthalene

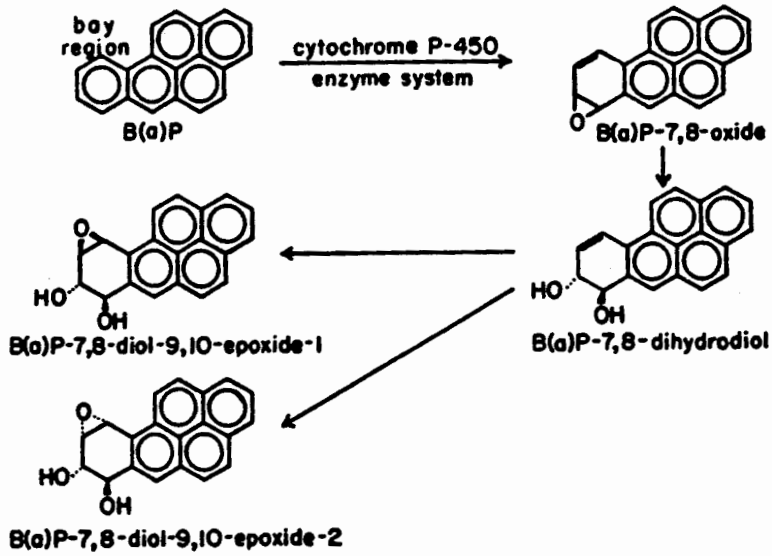

Fig. 1. Metabolic activation of B(a)P to bay region diol epoxides (Thakker *et al.* 1979).

Table IX. *Effects of PNAs on aquatic and terrestrial organisms.*

PNA	Organism	Concentration (mg/L) and/or response	Reference
Anthracene	*E. coli*	inhibit growth	Hass & Applegate (1975)
Phenanthrene	*E. coli*	inhibit growth	Hass & Applegate (1975)
Dibenz(a,c)anthracene	*E. coli*	inhibit growth	Hass & Applegate (1975)
Benz(a)anthracene	*E. coli*	stimulate growth	Hass & Applegate (1975)
Dibenz(a,h)anthracene	*E. coli*	stimulate growth	Hass & Applegate (1975)
Fluoranthene	*C. vulgaris, S. obliquus, A. oranunii*	stimulate growth at 0.01-0.02 ppm	Graf & Nowak (1966)
1,12-benzoperylene	*C. vulgaris, S. obliquus, A. oranunii*	stimulate growth at 0.01-0.02 ppm	Graf & Nowak (1966)
Indeno (1,2,3-cd) pyrene	*C. vulgaris, S. obliquus, A. oranunii*	stimulate growth at 0.01-0.02 ppm	Graf & Nowak (1966)
Benz(a)pyrene	*C. vulgaris, S. obliquus, A. oranunii*	stimulate growth at 0.01-0.02 ppm	Graf & Nowak (1966)
Dibenz(a,h)anthracene	sludge microorganisms	inhibit respiration	Malaney *et al.* (1967)
Dibenz(a,h)acridine	sludge microorganisms	inhibit respiration	Malaney *et al.* (1967)
Dibenz(a,j)acridine	sludge microorganisms	inhibit respiration	Malaney *et al.* (1967)
7-methylbenz(a) anthracene	sludge microorganisms	inhibit respiration	Malaney *et al.* (1967)
Benz(a)pyrene	newt	tumor induction	Arffman & Christensen (1961)
Benz(a)pyrene	clawed toad (*Xenopus laevis*)	tumor induction	Balls (1964)
Pyrene	chinook salmon	1.0 (lethal in 9-13 hr)	Macphee & Ruelle (1969)
3-methylcholanthrene	chinook and Coho salmon	10 (no effect)	Macphee & Ruelle (1969)
Pyridine	fish	15 (nervous system)	McKee & Wolf (1963)
Quinoline	trout	5.0 (lethal in 14 hr)	McKee & Woff (1963)
Quinoline	ciliates	750 (lethal)	McKee & Wolf (1963)

Poglazova *et al.* (1967 b) demonstrated very poor transformations of B(a)P by liquid cultures of *Bacillus megaterium* after 4 days incubation. One strain (N 13) transformed 53% B(a)P in 4 days. They showed that soil bacteria cultivated on agar which did not contain aromatic hydrocarbons lose the ability to destroy B(a)P. With soil inoculation of B(a)P and *Bacillus megaterium*, a strain not cultivated on B(a)P transformed 66% in 8 days, while a strain cultivated in the presence of B(a)P transformed 82% during the same time period.

Differences in the rates of transformation between soils and aqueous systems were noted. All of the investigated strains destroyed B(a)P to a greater extent in soil than in meat infusion agar. Strain N 5, which manifested no activity toward B(a)P in liquid culture, was very active in degrading the PNA in the contaminated soil from which it was isolated (Poglazova *et al.* 1967 b).

Poglazova *et al.* (1967 b) also demonstrated the oxidation of B(a)P in liquid cultures by *Mycobacterium* and a non-spore forming mutant of *Bacillus megaterium*. The great differences between strains of *Bacillus megaterium, Mycobacteria*, and mutant *Bacillus megaterium* suggest that the ability of microorganisms to transform B(a)P is a function of the strain and not the species.

Bacterial inoculation of sterile soil containing 20 μg B(a)P/g soil achieved significant reductions in the PNA concentration. Reduction of B(a)P ranged from 55 to 60% over the 8 day incubation period for pure cultures and increased to 84% when the two single strains PBK 13 and PBK 5 were combined in soil (Poglazova *et al.* 1967 a).

Poglazova *et al.* (1968) demonstrated that the rate of B(a)P transformation in liquid media is a function of the concentration. The % destroyed after 4 days remained relatively constant (45, 46, 33%) while the initial concentration increased 23-fold (2.0, 10.0, 46.0 μg/ml, respectively).

Bacterial inoculation of *B. megaterium* and two other strains that were acclimated to high B(a)P concentrations into sterile soil containing 130 mg/kg B(a)P resulted in 80 to 85% reduction in 8 days. These figures compare with 55 to 84% reductions in inoculated soil at 20 mg/kg. Thus the percentage B(a)P transformed remained approximately stable while the concentration was increased by a factor of seven. The rate of B(a)P transformation in soils is, therefore, shown to be a function of the soil concentration of B(a)P.

Khesina *et al.* (1969) investigated the degradation of B(a)P in soils under natural conditions of temperature and soil moisture. A control soil (C) with no history of pollution, a moderately polluted soil (M), and a highly oil-contaminated soil (N) were studied. Also a control soil with B(a)P added to increase the level to that of the (N) soil was included (B). The experiment was conducted in an unheated greenhouse for 3 mon. Water was added during the first and third months only. The results are presented in Table XVI.

Results clearly show that the degradation of B(a)P can be obtained under natural conditions and with natural soil microbial populations. Under natural conditions, as with laboratory results discussed previously, the rate of transformation appears to be a function of the soil concentration for soils that are

Table XVI. *Degradation of benzo(a)pyrene by soil microorganisms* (Khesina *et al.* 1969).

Soil	C_o [a]	B(a)P content of soil: 1 mon exposure (μg/kg soil)	2 mon exposure (μg/kg soil)	3 mon exposure (μg/kg soil)	Reduction at 3 mon (%)
C[b]	9.5	7.4	7.5	6.3	33
M[c]	545	377	346	159	71
B[d]	29,200	29,300	29,000	30,100	0
N[e]	28,500	16,000	16,700	13,700	52

[a] C_o = initial soil concentration (μg/g soil).
[b] C = control soil with no history of pollution.
[c] M = moderately oil-polluted soil.
[d] B = control soil with B(a)P added to increase the level to that of the (N) soil.
[e] N = highly oil-contaminated soil.

acclimated to the presence of PNAs. Soils (M) and (N) achieved similar reductions in B(a)P over 3 mon although initial soil levels of B(a)P differed by a factor of 50. For non-acclimated soils reductions in B(a)P were very low, some soils showing no reduction in B(a)P. Thus B(a)P can be microbially degraded in soil systems under natural conditions provided that the soil has been acclimated, *i.e.*, exposed to the presence of PNAs over a time period before introduction of additional PNA. Under these conditions for degradation, the rate of transformation appears to be a function of the soil concentration of B(a)P.

The growth and viability of soil bacteria does not appear to be affected by even high levels of B(a)P (Poglazova *et al.* 1967 a). Bacteria were shown to accumulate B(a)P primarily in lipid and other intracellular inclusions.

Table XVII summarizes the degradation of PNAs in soil systems. Information from a variety of sources was normalized with respect to kinetic parameters for describing PNA degradation as a function of soil concentration. Initial concentrations, rate constants, rates of transformation, and half-lives were calculated (Sims 1982).

From information obtained in Table XVII and from laboratory experiments conducted at North Carolina State University (Sims 1982) initial rates of transformation of PNA compounds in soil as a function of initial soil concentrations assuming first order kinetics are presented in Figure 6. These data were corrected for variations in temperature using an Arrhenius equation with coefficients developed from PNA data to a temperature of 20°C, $\theta = 1.013$. Rates were normalized to μg PNA transformed/g soil-dry wt/hr. The general trends shown in Figure 6 can be summarized as follows: (1) for a given PNA compound the initial rate of transformation increases with increasing initial soil concentration, (2) within the class of polycyclic aromatic compounds, the initial rate of transformation decreases with increasing number of fused benzene rings (or molecular size).

Table XVII. *Kinetic parameters describing rates of degradation of aromatic compounds in soil system.*

PNA	Initial concentration (μg/g soil)	k (day^{-1})	Rate of transformation (μg/g-day)	$t_{1/2}$[a] (days)		Reference
Pyrocatechol	500	3.47	1,735	0.2	m	Medvedev & Davidov (1972)
Phenol	500	0.693	364.5	1.0	m	Medvedev & Davidov (1972)
Phenol	500	0.315	157.5	2.2	l	Medvedev & Davidov (1972)
Fluorene	0.9	0.018	0.016	39	m	Groenewegen & Stolp (1976)
Fluorene	500	0.347	173.3	2	m	Medvedev & Davidov (1972)
Indole	500	0.693	364.5	1.0	m	Medvedev & Davidov (1972)
Indole	500	0.315	157.5	2.2	l	Medvedev & Davidov (1972)
Naphthol	500	0.770	385	0.9	m	Medvedev & Davidov (1972)
Naphthalene	7.0	5.78	40.4	0.12	m	Herbes & Schwall (1978)
Naphthalene	7.0	0.005	0.035	125	l	Herbes & Schwall (1978)
Naphthalene	25,000	0.173	4,331	4	h	Sisler & Zobell (1947)
1,4-Naphthoquinone	500	0.578	288.8	1.2	m	Medvedev & Davidov (1972)
Acenaphthene	500	0.173	86.6	4	m	Medvedev & Davidov (1972)
Acenaphthene	5	2.81	22.6	0.3	m	Medvedev & Davidov (1972)
Anthracene	3.4	0.21	0.714	3.3	l	Gardner *et al.* (1979)
Anthracene	13.7	0.004	0.054	175	m	Gardner *et al.* (1979)
Anthracene	10.3	0.005	0.050	143	m	Gardner *et al.* (1979)
Anthracene	11.4	0.006	0.073	108	m	Gardner *et al.* (1979)
Anthracene	40.0	0.005	0.208	138	m	Gardner *et al.* (1979)
Anthracene	36.4	0.005	0.196	129	m	Gardner *et al.* (1979)
Anthracene	25,000	0.198	4,950	3.5	h	Sisler & Zobell (1947)
Phenanthrene	2.1	0.027	0.056	26	m	Groenewegen & Stolp (1976)
Phenanthrene	25,000	0.277	6,930	2.5	h	Sisler & Zobell (1947)
Carbazole	500	0.067	33	10.5	m	Medvedev & Davidov (1972)
Carbazole	5	0.231	1.16	3	m	Medvedev & Davidov (1972)

Anthracene	3.4	0.21	0.714	3.3	l	Gardner et al.
Anthracene	13.7	0.004	0.054	175	m	Gardner *et al.* (1979)
Anthracene	10.3	0.005	0.050	143	m	Gardner *et al.* (1979)
Anthracene	11.4	0.006	0.073	108	m	Gardner *et al.* (1979)
Anthracene	40.0	0.005	0.208	138	m	Gardner *et al.* (1979)
Anthracene	36.4	0.005	0.196	129	m	Gardner *et al.* (1979)
Anthracene	25,000	0.198	4,950	3.5	h	Sisler & Zobell (1947)
Phenanthrene	2.1	0.027	0.056	26	m	Groenewegen & Stolp (1976)
Phenanthrene	25,000	0.277	6,930	2.5	h	Sisler & Zobell (1947)
Carbazole	500	0.067	33	10.5	m	Medvedev & Davidov (1972)
Carbazole	5	0.231	1.16	3	m	Medvedev & Davidov (1972)
Acridine	500	0.075	37.67	9.2	m	Medvedev & Davidov (1972)
Acridine	5	0.281	1.16	3	m	Medvedev & Davidov (1972)
Benz(a)anthracene	0.12	0.046	0.005	15.2	l	Herbes & Schwall (1978)
Benz(a)anthracene	0.12	0.0001	0.00001	6,250	m	Herbes & Schwall (1978)
Benz(a)anthracene	3.5	0.007	0.024	102	m	Groenewegen & Stolp (1976)
Benz(a)anthracene	20.8	0.003	0.062	231	m	Gardner *et al.* (1979)
Benz(a)anthracene	25.8	0.005	0.134	133	m	Gardner *et al.* (1979)
Benz(a)anthracene	17.2	0.008	0.060	199	m	Gardner *et al.* (1979)
Benz(a)anthracene	22.1	0.006	0.130	118	m	Gardner *et al.* (1979)
Benz(a)anthracene	42.6	0.003	0.118	252	m	Gardner *et al.* (1979)
Benz(a)anthracene	72.8	0.004	0.257	196	m	Gardner *et al.* (1979)
Benz(a)anthracene	25,000	0.173	4,331	4	h	Sisler & Zobell (1947)
Fluoranthene	3.9	0.016	0.061	44	m	Groenewegen & Stolp (1976)
Fluoranthene	18.8	0.004	0.072	182	m	Gardner *et al.* (1979)
Fluoranthene	23.0	0.007	0.152	105	m	Gardner *et al.* (1979)
Fluoranthene	16.5	0.005	0.080	143	m	Gardner *et al.* (1979)
Fluoranthene	20.9	0.006	0.125	109	m	Gardner *et al.* (1979)
Fluoranthene	44.5	0.004	0.176	175	m	Gardner *et al.* (1979)
Fluoranthene	72.8	0.005	0.379	133	m	Gardner *et al.* (1979)
Pyrene	3.1	0.020	0.061	35	m	Groenewegen & Stolp (1976)
Pyrene	500	0.067	33	10.5	m	Medvedev & Davidov (1972)
Pyrene	5	0.231	1.16	3	m	Medvedev & Davidov (1972)
Chrysene	4.4	0	0	–		Groenewegen & Stolp (1976)
Chrysene	500	0.067	33	10.5	m	Medvedev & Davidov (1972)
Chrysene	5	0.126	0.63	5.5	m	Medvedev & Davidov (1972)
Benz(a)pyrene	0.048	0.014	0.007	50	l	Herbes & Schwall (1978)
Benz(a)pyrene	0.01	0.001	0.00001	694	l	Herbes & Schwall (1978)
Benz(a)pyrene	3.4	0.012	0.041	57	m	Groenewegen & Stolp (1976)
Benz(a)pyrene	9.5	0.002	0.022	294	m	Gardner *et al.* (1979)
Benz(a)pyrene	12.3	0.005	0.058	147	m	Gardner *et al.* (1979)

Table XVII (*continued*)

PNA	Initial concentration (μg/g soil)	k (day^{-1})	Rate of transformation (μg/g-day)	$t_{1/2}$[a] (days)		Reference
Benz(a)pyrene	7.6	0.003	0.020	264	m	Gardner *et al.* (1979)
Benz(a)pyrene	18.5	0.023	0.312	30	m	Gardner *et al.* (1979)
Benz(a)pyrene	17.0	0.002	0.028	420	m	Gardner *et al.* (1979)
Benz(a)pyrene	32.6	0.004	0.129	175	m	Gardner *et al.* (1979)
Benz(a)pyrene	1.0	0.347	0.347	2	h	Shabad *et al.* (1971)
Benz(a)pyrene	0.515	0.347	0.179	2	h	Shabad *et al.* (1971)
Benz(a)pyrene	0.00135	0.139	0.0002	5	h	Shabad *et al.* (1971)
Benz(a)pyrene	0.0094	0.002	0.00002	406	l	Shabad *et al.* (1971)
Benz(a)pyrene	0.545	0.011	0.006	66	l	Shabad *et al.* (1971)
Benz(a)pyrene	28.5	0.019	0.533	37	l	Shabad *et al.* (1971)
Benz(a)pyrene	29.2	0	0	–		Shabad *et al.* (1971)
Benz(a)pyrene	9,100	0.018	161.7	39	h	Lijinsky & Quastel (1956)
Benz(a)pyrene	19.5	0.099	1.93	7	h	Poglazova *et al.* (1967 b)
Benz(a)pyrene	19.5	0.139	2.70	5	h	Poglazova *et al.* (1967 b)
Benz(a)pyrene	19.5	0.231	4.50	3	h	Poglazova *et al.* (1967 b)
Benz(a)pyrene	130.6	0.173	22.63	4	h	Poglazova *et al.* (1968)
Benz(a)pyrene	130.6	0.116	15.08	6	h	Poglazova *et al.* (1968)
Dibenz(a,h)anthracene	9,700	0.033	320.1	21	h	Lijinsky & Quastel (1956)
Dibenz(a,h)anthracene	25,000	0.039	962.5	18	h	Sisler & Zobell (1947)

[a] l = low temperature range (< 15°C), m = medium temperature range (15-25°C), and h = high temperature range (> 25°C).

Fig. 6

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INITIAL RATE OF DEGRADATION (ug/g-hr.)

Benz(a)pyrene	19.5	0.231	4.50	3 h		Poglazova *et al.* (1967 b)
Benz(a)pyrene	130.6	0.173	22.63	4 h		Poglazova *et al.* (1968)
Benz(a)pyrene	130.6	0.116	15.08	6 h		Poglazova *et al.* (1968)
Dibenz(a,h)anthracene	9,700	0.033	320.T	21 h		Lijinsky & Quastel (1956)
Dibenz(a,h)anthracene	25,000	0.039	962.5	18 h		Sisler & Zobell (1947)

[a] l = low temperature range (< 15°C), m = medium temperature range (15-25°C), and h = high temperature range (> 25°C).

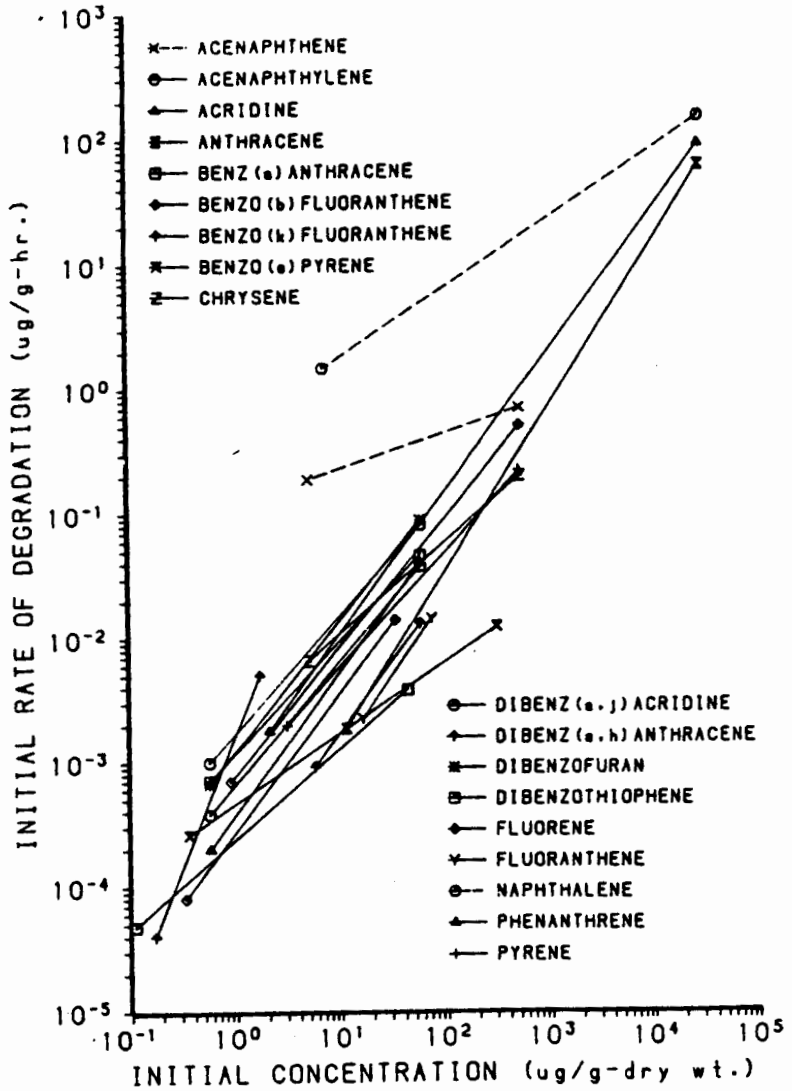

Fig. 6. Rates of transformation on PNA compounds in soil as a function of initial soil concentrations (Sims 1982).

III. Photodecomposition, oxidation, and hydrolysis of PNAs

PNAs, in general, absorb solar radiation strongly and therefore undergo direct photolysis (Radding *et al.* 1976). Table XVIII summarizes photodecomposition information for several PNAs.

PNAs photodecompose readily in the atmosphere by reaction with ozone, other oxidants, nitrogen oxides, and sulfur oxides (NAS 1972). Studies by Southworth (1977), Suess (1972 a), and Andleman and Suess (1971) indicated that PNA photodecomposition in aqueous environments is influenced by water depth, turbidity, solar radiation intensity (seasonal and diurnal fluctuations), temperature, and dissolved oxygen. Reduction of B(a)P under water treatment plant conditions with ultraviolet (UV) radiation amounted to 60 to 80% with 2.5 min of irradiation, and 80 to 90% with 15 min of irradiation (Il'Nitskii *et al.* 1971). The mechanism of photodecomposition for the degradation of PNAs in sediments, sludges, and deposits is believed to be relatively unimportant due to lack of radiation and oxygen beneath surface layers.

The effects of sunlight and UV on photodecomposition of dimethylbenzanthracene (DMBA), B(a)P, and benz(a)anthracene (B(a)A) were investigated by Paalme and Gubergrits (1972). The presence of O_2 had a greater effect than the presence of N_2. For PNAs in general the singlet oxygen is the oxidant and the reaction products include quinones (NAS 1972, Stevens and Algar 1968).

Mailath *et al.* (1974) demonstrated the influence of active surfaces on B(a)P photodecomposition. Sunlight destroyed 65 to 95% in 5 hr with B(a)P on thin silica gel layers. With glass surfaces a 100-fold reduction in sunlight decomposition was observed. Rohrlich and Suckow (1973) obtained 80% degradation of B(a)P adsorbed to silica gel and recovered 13 photodecomposition products, including quinones.

Detoxication of PNAs by irradiation has been investigated to a limited ext[illegible] While Suess (1972 b) observed that irradiation products of B(a)P seemed no[illegible] be carcinogenic to mice, Graf and Haller (1977) reported that UV degradation products of B(a)P retained 50% of the original toxicity in a microbiological test for carcinogenicity using *Tetrahymena pyriformis*.

The effect of solvents and surfactants on photodecomposition of PNAs has also been investigated (Borneff and Knerr 1959, Suess 1972 a, Paalme *et al.* 1975, and Boyland 1933). Generally, increasing the solubilities of PNAs results in an increase in the extent and rate of photodecomposition. The presence of phenols in aqueous PNA solutions has been shown to increase the rate of photochemical oxidation (Karu *et al.* 1973), and to inhibit the extent of photochemical oxidation (Gubergrits *et al.* 1972).

Photodecomposition of PNAs has also been observed to be influenced by the presence of other PNAs. B(a)P photolysis was increased in the presence of B(e)P (Paalme and Gubergrits 1974), DMBA (Paalme *et al.* 1976), and 3-methylcholranthrene (Paalme and Gubergrits 1976). However, in the same study, pyrene decreased B(a)P photolysis.

While singlet oxygen is considered to be the major oxidant species generated by the direct photolysis of PNAs, other principal oxidizing species in natural aqueous systems include alkylperoxy ($RO_2\cdot$) and hydroperoxy ($HO_2\cdot$) radicals generated by photolytic cleavage of trace carbonyl compounds or from enzymatic sources (Versar 1979). Free radical oxidation of PNAs are summarized by

Radding *et al.* (1976). Half-lives for the reaction of $RO_2\cdot$ radical with anthracene, B(a)P, and perylene have been calculated to be 1,600, 9,900, and 1,600 days, respectively, for a 10^{-10} molar steady-state concentration for the $RO_2\cdot$ radical for average daily illumination in natural waters (Radding *et al.* 1976).

Hydrolysis is not considered to be an important mechanism for degradation of PNAs in the environment. Polycyclic aromatic hydrocarbons do not contain groups amenable to hydrolysis (Radding *et al.* 1976).

Photodecomposition, oxidation, and hydrolysis of PNA compounds are not considered as significant pathways for PNA degradation in soil environments.

IV. Volatilization of PNAs

Volatilization half-lives for most PNAs are not known. Table XIX summarizes available information for several PNAs. The rate of volatilization from aqueous environments is influenced by properties of the compound (Henry's law constant) and the environment (wind, water turbulence, and temperature) (Southworth 1977).

Volatilization is considered more important under environmental conditions characterized by shallow, clear, agitated natural waters. Methods for predicting volatilization rates from natural aqueous systems using theoretical considerations (Mackay and Wolkoff 1973, Mackay and Leinonen 1975) require substantial measured physical data and are not considered practical for many conditions (Versar 1979). Southworth (1977) employed a simple first-order exponential decay equation and considered Henry's Law constants, gas phase exchange, and liquid phase exchange for the environmental conditions listed above. He concluded that volatilization of polycyclic aromatic hydrocarbons with four or more rings is expected to be insignificant in any sizeable water body due to the low Henry's Law constants. Although volatilization of some high molecular weight, low-water-soluble organics has been shown to be significant due to high activity coefficients (Mackay and Wolkoff 1973), volatilization is not considered to be an important transport and removal process for PNAs (Versar 1979, Southworth 1977) (refer to Table II for vapor pressure for PNAs).

Smith *et al.* (1978) state that when PNAs are sorbed onto sediments, volatilization of the sorbed PNAs is presumed to be very slow. The relatively high log octanol:water partition coefficients of most PNAs indicate that an adsorption mechanism is much more important in determining the fate of PNAs in terrestrial systems than volatilization.

V. Soil adsorption, leaching, and run-off

Adsorption and leaching characteristics of PNAs in soils and sediments are needed to predict their movement and fate in terrestrial and aquatic environments. Adsorption of nonionic, nonpolar chemicals by solid surfaces and movement through porous media depends upon chemical properties of the compound

Table XVIII. *Photodecomposition of PNAs.*

PNA compound	Comments and $t_{1/2}$	Reference
Naphthalene	absorbs solar radiation strongly	Versar (1979)
Anthracene	$t_{1/2}$ = 35 min, midday sunlight, midsummer, 35°N latitude	Southworth (1977)
Fluorene	absorbs solar radiation strongly	Versar (1979)
Acenaphthylene	absorbs solar radiation strongly	Versar (1979)
Acenaphthene	absorbs solar radiation strongly	Versar (1979)
Phenanthrene	absorbs solar radiation strongly	Versar (1979)
Benz(a)anthracene	$t_{1/2}$ = 4.8 hr, winter, 35°N latitude	Southworth (1977)
	UV degradation creates quinones	McGinnes & Snoeyink (1974)
Chrysene	absorbs solar radiation strongly	Versar (1979)
Pyrene	absorbs solar radiation strongly	Versar (1979)
Fluoranthene	absorbs solar radiation strongly	Versar (1979)
Benz(a)pyrene	$t_{1/2}$ = 1 hr, midday, winter	Smith *et al.* (1978)
	adsorption to kaolinite clay inhibits photolysis	Lu *et al.* (1977)
	$t_{1/2}$ = 11 hr (21°C, O_2) with fluorescent light on B(a)P adsorbed on calcite and suspended in water	Suess (1972 a)
	$t_{1/2}$ = 20 hr with UV radiation	Rondia & Epstein (1968)
	surfactants increase photolysis rates	Paalme *et al.* (1975)
	$t_{1/2}$ = 5.3 hr in presence of UV and without O_3	Lane & Katz (1977)
	$t_{1/2}$ = 0.2 hr in presence of both UV and O_3	Lane & Katz (1977)
Benzo(k)fluoranthene	absorbs solar radiation strongly	Versar (1979)
Dibenz(a,h)anthracene	absorbs solar radiation strongly	Versar (1979)
7,12-Dimethylbenzanthracene	absorbs solar radiation strongly; main product is epoxide; rate is function of solvent, wave length and intensity	Versar (1979) Lopp *et al.* (1976)

	in water	
	$t_{1/2}$ = 20 hr w. V radiation	Rondia & Epstein (1968)
	surfactants increase photolysis rates	Paalme *et al.* (1975)
	$t_{1/2}$ = 5.3 hr in presence of UV and without O_3	Lane & Katz (1977)
	$t_{1/2}$ = 0.2 hr in presence of both UV and O_3	Lane & Katz (1977)
Benzo(k)fluoranthene	absorbs solar radiation strongly	Versar (1979)
Dibenz(a,h)anthracene	absorbs solar radiation strongly	Versar (1979)
7,12-Dimethylbenzanthracene	absorbs solar radiation strongly; main product is epoxide; rate is function of solvent, wave length and intensity	Versar (1979) Lopp *et al.* (1976)
3-Methylcholanthrene	rate catalyzed by dimethyl sulfoxide solvent	Dao *et al.* (1971)
Benzo(k)fluoranthene	absorbs solar radiation strongly	Versar (1979)
Benzo(ghi)perylene	absorbs solar radiation strongly	Versar (1979)
Indeno(1,2,3-cd)pyrene	absorbs solar radiation strongly	Versar (1979)

Table XIX. *Volatilization of PNAs.*

PNA compound	Comments and $t_{1/2}$	Reference
Naphthalene	Vapor pressure high (important process)	Versar (1979)
Anthracene	$t_{1/2}$ = 300 hr under quiescent conditions in water 1 m deep	Southworth (1977)
	$t_{1/2}$ = 18 hr under agitation	Southworth (1977)
Fluorene	not important process	Versar (1979)
Acenaphthalene	not important process	Versar (1979)
Acenaphthene	not important process	Versar (1979)
Phenanthrene	not important process	Versar (1979)
Benz(a)anthracene	$t_{1/2}$ = 90 hr; rate constant 0.00789 hr^{-1}	Smith *et al.* (1978)
Chrysene	not important process	Versar (1979)
Pyrene	not important process	Versar (1979)
Fluoranthene	not important process	Versar (1979)
Benz(a)pyrene	$t_{1/2}$ = 22 hr with agitation; rate constant 0.030 hr^{-1} adsorption reduces volatilization significantly	Smith *et al.* (1978)
Benzo(f)fluoranthene	not important process	Versar (1979)
Dibenz(a,h)anthracene	not important process	Versar (1979)
Benzo(k)fluoranthene	not important process	Versar (1979)
Benzo(ghi)perylene	not important process	Versar (1979)
Indeno(1,2,3-cd)pyrene	not important process	Versar (1979)

Table XX. *Adsorption of PNAs by activated carbon and by soils and sediments.*

PNA	Log K_p[a]	Adsorbent: Activated carbon[b] K	Activated carbon[b] 1/n	Soils and sediments K	Soils and sediments K_{oc}
Benzene	–	1.0	1.60	0.13[e]	83[d]
Toluene	–	26.1	0.44	–	–
Quinoline	–	–	–	10.9[d]	–
Naphthalene	3.37	132	0.42	–	1,300[d]
2-Methylnaphthalene	–	–	–	–	8,500[d]
Benzo(b)thiophene	–	–	–	50	–
Anthracene	4.45	376	0.70	0.01-0.05[c]	26,000[d]
Benzo(f)quinoline	–	–	–	1,313	–
Acenaphthylene	4.07	115	0.37	–	–
Acenaphthene	4.33	190	0.36	–	–
Phenanthrene	4.46	215	0.44	–	23,000[d]
Fluorene	4.18	330	0.28	–	–
9H-carbazole	–	–	–	175[d]	–
Fluoranthene	5.33	664	0.61	–	–
Tetracene	–	–	–	–	650,000[d]
Pyrene	5.32	–	–	–	84,000[d]
Benz(a)anthracene	5.61	–	–	26,200[d]	–
Dibenzothiopene	–	–	–	137[g]	10,240 (mean)[g]
3 [illegible]hylcholanthrene	6.97	–	–	18,196(mean)[f]	1,789,000 (mean)[f]
1 [illegible](b)fluoranthene	6.57	57	0.37	–	–
Benzo(k)fluoranthene	6.84	181	0.57	–	–
Benz(a)pyrene	6.04	33.6	0.44	76,000[d]	4,510,651(mean)[d]
Dibenz(a,h)anthracene	5.97	69.3	0.75	22,774(mean)[f]	2,029,000(mean)[f]
Benzo(ghi)perylene	7.23	10.7	0.37	–	–
7H-dibenzocarbazole	–	–	–	26,233(mean)[d]	–

[a] Versar (1979).
[b] Dobbs & Cohen (1980).
[c] Herbes (1977).
[d] Reinbold *et al.* (1978).
[e] McBride *et al.* (1975).
[f] Means *et al.* (1980).
[g] Hassett *et al.* (1980).

(adsorbate) and the characteristics of the solid surface (adsorbent). Thus organic matter presence is highly correlated with adsorption. Water soluble compounds tend to migrate in soil and aquatic systems and are not significantly adsorbed. However, more hydrophobic compounds become readily adsorbed to lipophilic organic matter in soils and, as a result, become relatively non-mobile.

Reinbold *et al.* (1978) summarized the adsorption of energy-related pollutants in the environment. A review of the literature on the adsorption of pollutants on sediments and soils revealed that, except for pesticides, most sorption information for organic chemicals was obtained using adsorbents other than soils, sediments, and clay minerals. Adsorption constants were most often derived by use of Freundlich or Langmuir adsorption equations.

The mechanism of adsorption is used to explain the bioavailability of organic chemicals between different soils or different classes of chemicals (Bailey and White 1964). Major factors influencing adsorption in soil systems include soil type, physicochemical properties of the chemicals, soil moisture, temperature, presence of competing molecules, solvents, and pH.

Table XX summarizes adsorption information for several PNAs. Included are octanol-water partition coefficients, Freundlich activated carbon isotherm results (adsorption capacity (K) and adsorption intensity (l/n)), and soil/sediment adsorption results using the Freundlich equation (adsorption capacity (K) and an adjustment of capacity based on organic carbon content (K_{oc})). The Freundlich equation can be expressed as

$$X/M = K\,C_f^{1/n}$$

where

X/M = unit adsorbate removed from solution/unit adsorbent,
C_f = amount of adsorbate remaining in the treated water at equilibrium,
K = a coefficient describing the adsorption capacity, and
l/n = indication of adsorption intensity.

When adsorption is normalized with respect to organic carbon (OC) content of the adsorbent, the form of the equation used is

$$K_{oc} = \frac{(K)\,(100)}{\%\,OC}$$

McBride *et al.* (1975) investigated the adsorption of benzene on smectite (Wyoming montmorillonite) as a function of organophilic cation and water content. Results are presented in Table XXI. Competition between water and the aromatic molecules has the most obvious effect on adsorption of benzene. Langmuir adsorption isotherm results indicated a maximum benzene adsorption with TMA+-montmorillonite of 13.2 g benzene/100 g adsorbent.

The sorption of pyrene, 7,12-dimethylbenzanthracene, 3-methylcholanthrene, and dibenz(a,h)anthracene on 14 soil/sediment samples was investigated by Means *et al.* (1980). Results for soil/sediment characteristics and PNA adsorption

are summarized in Table XXII. Freundlich equilibrium constants (K_d) were obtained and since the isotherms were linear, the data were fitted to a simplified equation:

$$C_s = K C_w$$

The resulting partition constants (K) are presented in Table XXII. The sorption constants (K), when normalized to organic carbon content of the adsorbent (K_{oc}), were predictive of the octanol-water partition coefficient for the PNAs listed:

$$\log K_{oc} = \log K_{ow} - 0.317$$

where K_{ow} indicates the octanol-water partition coefficient.

Although many soil/sediment characteristics were determined, including pH, CEC, total N, organic carbon, and sand, silt, and clay content, the only significant relationship found was that between K and percent organic carbon of the adsorbent (Table XXII). K_{oc} has been shown to be a unique constant for non-polar compounds (Karickhoff *et al.* 1979, Means *et al.* 1979, Means *et al.* 1980).

The order of increasing adsorption to the soils/sediments is: pyrene < 7,12-dimethylbenzanthracene < 3-methylcholanthrene < dibenz(a,h)anthracene. The increase in sorption of these PNAs appears to be more closely related to increases in effective chain length of the molecule than to increases in mass alone.

The important role of organic matter versus mineral particulates was emphasized by Herbes (1977). Adsorption of 0.02 μg/L anthracene by montmorillonite concentrations of 10 to 100 mg/L ranged from one to 5%. Adsorption of anthracene by autoclaved yeast cells under identical conditions results in 10 to 50% uptake. The heat of adsorption to the organic matter (yeast cells) was 5.2 kcal/mole indicating a physical adsorption process.

The influence of soil type on adsorption of pyrene was investigated by Karickhoff *et al.* (1979). They calculated the partition coefficient (K_p) and the correction for organic carbon (K_{oc}) for each soil type. Results are presented in Table XXIII. The significant role of the organic carbon in soil in PNA adsorption is obvious.

Table XXI. *Benzene adsorption on Wyoming montmorillonite* (McBride *et al.* 1975).

	Benzene adsorbed (g/100 g)	
Exchange form of Smectite	From vapor (no water)	From aq solution (350 mg/L)
Cu^{2+}	18.8	0.6
Tetramethylammonium (TMA^+)	22.6	7.2
Tetraethylammonium (TEA^+)	14.2	1.8
Tetrapropylammonium (TPA^+)	13.8	0.0

Table XXII. *Soil and sediment properties and sorption constants for PNAs* (Means *et al.* 1980).

Soil and sediment properties				PNA adsorption characteristics							
				Pyrene		DMBA		3-MC		DB(a,h)A	
Type	CEC (meq/100g)	Organic carbon (%)	Clay (%)	K_p	K_{oc}	K_p	K_{oc}	K_p	K_{oc}	K_p	K_{oc}
B2	3.72	1.21	18.6	760	62,860	2,371	195,998	15,140	1,251,210	20,461	1,690,971
4	23.72	2.07	55.2	1,065	51,469	2,648	127,812	30,085	1,453,404	34,929	1,687,404
5	19.00	2.28	31.0	1,155	50,650	5,210	228,499	8,273	362,845	18,361	805,292
6	33.01	0.72	68.6	814	85,256	1,346	186,986	15,820	2,197,250	19,882	2,622,453
8	3.72	0.15	8.8	101	67,467	611	407,496	2,257	1,504,538	1,759	1,172,847
9[a]	12.40	0.11	17.4	71	64,706	1,028	934,225	2,694	2,449,190	2,506	2,277,875
14[a]	18.86	0.48	63.6	277	57,763	562	117,161	30,627	6,380,703	14,497	3,020,262
15	11.30	0.95	35.7	788	82,421	3,742	393,907	23,080	2,429,456	25,302	2,663,317
18	15.48	0.66	39.5	504	76,816	1,895	287,196	20,642	3,127,521	20,192	3,059,425
20[a]	8.50	1.80	28.0	723	59,946	1,617	124,347	16,231	1,248,534	7,345	565,014
21	8.33	1.88	7.1	1,119	59,515	5,576	296,580	24,506	1,303,532	55,697	2,962,603
22	8.58	1.67	21.2	806	48,236	2,679	160,801	20,972	1,255,821	39,809	2,383,765
23	31.15	2.38	69.1	1,043	43,897	6,777	284,743	17,127	719,693	19,254	808,991
26	20.86	1.48	42.9	994	67,189	8,740	252,735	37,364	2,524,581	30,840	2,691,870

[a] Soils; all others are sediments.

Table XXIII. *Adsorption of pyrene and dibenzothiophene to soils.*

Soil		Pyrene adsorption characteristics[a]	
Type	Organic carbon (%)	K_p	K_{oc}
Hickory Hill			
sand	0.18	42	32,000
coarse silt	3.27	3,000	92,000
medium silt	1.98	2,500	1,300,000
fine silt	1.34	1,500	1,100,000
clay	1.20	1,400	1,200,000
Sample		**Dibenzothiophene adsorption characteristics[b]**	
		K_p	K_{oc}
B2		117.5	9,711
4		180.6	8,725
5		167.1	7,329
6		60.8	8,444
8		9.4	6,267
9		5.8	5,273
14		49.7	10,354
15		179.9	18,937
18		65.1	9,864
20		101.4	7,800
21		276.0	14,681
22		176.3	10,557
23		388.6	16,328
26		134.5	9,088

[a] Karickhoff *et al.* (1979).
[b] Hassett *et al.* (1980).

The influence of soil characteristics on adsorption of dibenzothiophene was investigated by Hassett *et al.* (1980). They calculated the partition coefficient (K_p) and the correction for organic matter (K_{oc}) for each sample. Results are presented in Table XXIII. Again the significant role of the organic carbon in soil in PNA adsorption is obvious.

VI. Plant uptake, effects, and metabolism of PNAs

a) Natural background concentration of PNAs in vegetation

PNAs are ubiquitous constituents of crops, plants, and algae in the natural environment including urban and pristine areas. Natural background levels of PNAs reported for various plants and crops are summarized in Table XXIV. In

Table XXIV. *Natural background levels of PNAs in plants/crops.*

PNA	Plant/crop	Concentration (μg/kg, dry wt)	Reference
Anthracene	Post oak (leaves)	70	Hancock *et al.* (1970)
Anthracene	Little Bluestem (leaves)	50	Hancock *et al.* (1970)
Fluoranthene	Little Bluestem (leaves)	33	Hancock *et al.* (1970)
Fluoranthene	Post oak (leaves)	62	Hancock *et al.* (1970)
Benz(a)anthracene	Little Bluestem (leaves)	22	Hancock *et al.* (1970)
Benz(a)anthracene	Post oak (leaves)	60	Hancock *et al.* (1970)
Pyrene	Little Bluestem (leaves)	58	Hancock *et al.* (1970)
Pyrene	Post oak (leaves)	88	Hancock *et al.* (1970)
Benz(a)pyrene	Little Bluestem (leaves)	30	Hancock *et al.* (1970)
Benz(a)pyrene	Post oak (leaves)	40	Hancock *et al.* (1970)
Benz(a)pyrene	Lettuce	12	Graf & Diehl (1966)
Benz(a)pyrene	Spinach	20	Graf & Diehl (1966)
Benz(a)pyrene	Endive	50	Graf & Diehl (1966)
Benz(a)pyrene	Potato peeling	0.36	Shabad & Cohan (1972)
Benz(a)pyrene	Potato tuber	0.09	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat seed	0.29	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat stem	27.0	Shabad & Cohan (1972)
Benz(a)pyrene	Winter rye seed	0.35	Shabad & Cohan (1972)
Benz(a)pyrene	Coffee green beans	0.60	Il'Nitskii & Cohan (1972)
Benz(a)pyrene	Young wheat plants	48-66	Siddiqi & Wagner (1972)
Benz(a)pyrene	Carrots	1.65-6.0	Il'Nitskii *et al.* (1974)
Benz(a)pyrene	Beets	0.6-2.0	Il'Nitskii *et al.* (1974)
Benz(a)pyrene	Cabbage	0.8-1.2	Il'Nitskii *et al.* (1974)
Benz(a)pyrene	Carrots	0.08-0.14	Siegfried (1975)
Benz(a)pyrene	Head lettuce	0.2-1.3	Siegfried (1975)
Benz(a)pyrene	Japanese radish root	0.01	Shiraishi & Takahatake (1974)

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Benz(a)pyrene	Carrots	0.08-0.14	Siegfried (1975)
Benz(a)pyrene	Head lettuce	0.2-1.3	Siegfried (1975)
Benz(a)pyrene	Japanese radish root	0.01	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Spinach	0.26-3.3	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Chrysanthemum	1.20	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Chinese cabbage	0.05	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Potato	0.01	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Carrot	0.02	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Onion	0.01	Shiraishi & Takabatake (1974)
Benz(a)pyrene	Sunflower oil, cottonseed oil, peanut oil, rapeseed oil	1-5	Grigorenko *et al.* (1970)
Benz(a)pyrene	Apple	0.02	Shiraishi (1975)
Benz(a)pyrene	Banana	0.02	Shiraishi (1975)
Benz(a)pyrene	Banana peel	0.03	Shiraishi (1975)
Benz(a)pyrene	Grape	0.02	Shiraishi (1975)
Benz(a)pyrene	Persimmon	0.02	Shiraishi (1975)
Benz(a)pyrene	Pineapple	0.02	Shiraishi (1975)
Benz(a)pyrene	Plum	0.04	Shiraishi (1975)
Benz(a)pyrene	Mandarin orange	0.03	Shiraishi (1975)
Benz(a)pyrene	Orange peel	0.15	Shiraishi (1975)

general leaves exhibit the largest PNA concentrations (22 to 88 ppb), and und ground vegetables including potatoes, carrots, onions, and radishes exhibit lowest PNA concentrations (0.01 to 6.0 ppb). The distribution of PNAs amo various categories of vegetation is approximately: tree leaves (22 to 88 ppb) cereals (48 to 66 ppb) > leafy vegetables (0.05 to 50 ppb) > underground ve tables (0.01 to 6.0 ppb) > fruits (0.02 to 0.04 ppb).

While the presence of background levels of PNAs in vegetation is read demonstrated (Table XXIV), the source and the relative contributions of diff ent possible sources of PNAs is the subject of much controversy and deba Atmospheric deposition of PNAs produced as a result of industrial processe considered the source of benz(a)pyrene (B(a)P) in soils and in vegetation n air fields (Smirnov 1970) and near urban areas (Kolar *et al.* 1975). Abo ground plant parts contained higher levels of B(a)P than parts beneath t ground. Also the amount of B(a)P was proportional to the exposed plant su face area. These studies indicate that atmospheric deposition is the source PNAs in vegetation rather than uptake from polluted soils. The degree of PN contamination of vegetables is often explained by surface area/kg, location, an exposure time (Grimmer and Hildebrand 1965).

Other researchers (Hancock *et al.* 1970, Graf and Diehl 1966, and Borneff *al.* 1968 a and b) have demonstrated that both higher and lower plants exhib background levels of PNAs independent of the area in which they are grow The presence of a 'base level' of PNAs in plants is attributed to biochemical syn thesis by the plant.

In addition to anthropogenic activities resulting in PNA deposition on plants and biochemical synthesis by plants, a third possible source of PNAs found i vegetation is plant-uptake from soil. Uptake of PNAs from aqueous and so media and from compost has been investigated by Kolar *et al.* (1975), Shaba and Cohan (1972), Shcherbak (1969), Wagner and Siddiqi (1970), Borneff *et al* (1973), Siegfried (1975), and Graf and Nowak (1966), among others. Unfortu nately, the major emphasis of research has been devoted to the study of B(a)P behavior, which does not always correlate with the behavior of other PNAs

The health implications of ingestion of plants with background PNA level are not known. Hakama and Saxen (1967) and others (NAS 1972) have demon strated correlations of human stomach cancer and high cereal consumption and ingestion of plants containing higher levels of PNAs. Wynder *et al.* (1963) attributed as significant the role of starchy foods with concomitant low intake of fresh fruits as the cause of cancer among vegetarians. However, because plant parts containing starch contain only one to 10% of the amount of PNA in leaves and green plant parts, the role and significance of plant or plant parts in the human diet is not known.

PNAs in soils and in wheat plant parts are summarized in Table XXV. With B(a)P, the crop/soil ratio for spring and summer wheat was lowest in seeds and much higher in stems and straw. Also the concentration of B(a)P in the plant parts was not a function of the soil concentration, as shown in Table XXV.

Overcash

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Table XXV. *PNAs in soils and in wheat.*

	Wheat		Soil	Crop	
PNA	Type	Concentration (μg/kg, dry wt)	Concentration (μg/kg, dry wt)	Soil	Reference
Benz(a)pyrene	Spring wheat-seed	0.29	1.6	0.18	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-seed	0.38	170	0.002	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-seed	0.84	1.6	0.53	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-seed	0.72	170	0.004	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-stem	4.52	1.6	2.9	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-stem	3.60	170	0.021	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-straw	27.0	1.6	17.0	Shabad & Cohan (1972)
Benz(a)pyrene	Spring wheat-straw	26.7	170	0.16	Shabad & Cohan (1972)
Benz(a)pyrene	Summer wheat-seed	3.0	2.0	1.5	Wagner & Siddiqi (1970)
Benz(a)pyrene	Summer wheat-seed	3.0	1,300	0.002	Wagner & Siddiqi (1970)
Benz(a)pyrene	Summer wheat-stem	15.0	2.0	7.5	Wagner & Siddiqi (1970)
Benz(a)pyrene	Summer wheat-stem	25.0	1,300	0.020	Wagner & Siddiqi (1970)
Benz(a)pyrene	Summer wheat-straw	7.0	2.0	3.5	Wagner & Siddiqi (1970)
Benz(a)pyrene	Summer wheat-straw	8.0	1,300	0.01	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-seed	76	4.4	17.0	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-seed	98	1,300	0.08	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-stem	100	4.4	2.30	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-stem	223	1,300	0.18	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-straw	104	4.4	24.0	Wagner & Siddiqi (1970)
3,4-Benzfluoranthene	Summer wheat-straw	220	1,300	0.18	Wagner & Siddiqi (1970)

When the soil concentration of B(a)P was increased, the plant concentration remained approximately the same. However, biomagnification of B(a)P for seed, stem and straw is demonstrated. With 3,4-benzfluoranthene, the pattern was not the same. Plant concentrations were generally much higher, with smaller differences among the plant parts. Also an increase in plant 3,4-benzfluoranthene content correlated with an increase in the soil PNA content. Biomagnification of 3,4-benzfluoranthene is demonstrated. Thus the two PNAs exhibited different behavior under similar soil and crop conditions. Biomagnification, however, is evident with both PNAs.

Soil and plant levels of PNAs as influenced by fertilizer type are presented in Table XXVI. For horseradish the crop/soil ratio is consistently lower for the root center and higher for the root skin, regardless of the method of fertilization. Interestingly, the crop/soil ratios tend to be as high or higher for non-fertilized and mineral fertilized soils as for compost and manure fertilized soils. With carrots, B(a)P content in the plant did not correlate with B(a)P content in the soil. Biomagnification is not indicated for any of the crops, as plant PNA content varied from 0.04% to 78% of the soil content.

Borneff *et al.* (1973) concluded that B(a)P content in food is small and is unrelated to compost origin or B(a)P content of the compost. PNA content in industrially prepared compost is given by Wagner and Vonderheid (1978). Only in the outer layer of plant roots does the B(a)P concentration correlate with the soil concentration (Borneff *et al.* 1973). Because of the small background and concentration in plants, the amount ingested with edible roots grown on compost-amended soil may not enhance the human health hazard.

Much information has been collected which indicates that many higher plants may not take up PNAs. Blum and Swarbrick (1977) studied uptake of radiolabeled ^{14}C-B(a)P by plants grown hydroponically in nutrient solutions containing 8.0 ppb B(a)P. Crops investigated included green beans, cantalopes, and cotton seeds. Results indicated that no (< 3 ppb) B(a)P was translocated or accumulated in any of the plants or plant tissues, including leaf and stem tissues for green beans.

b) Plant response to PNA additions

PNAs have been demonstrated to act like plant hormones, stimulating growth and yield of higher and lower plants. Table XXVII presents the results of the effect of B(a)P on algal cell size and summer rye kernel yield. Graf (1965) demonstrated the growth-promoting effects of PNAs with higher plants. Daily watering with B(a)P (10 μg/L) effected an increase in yield of kohlrabi (20%), cauliflower (20%), rye (300%), and tobacco (100%).

Graf (1965) also demonstrated that the growth promoting effect was proportional to the carcinogenic potential. Dibenz(a,h)anthracene which is a more potent carcinogen than benz(a)anthracene had a stronger growth-promoting effect on tobacco.

Table XXVI. *Average soil and plant levels of PNAs[a] as influenced by fertilizer type.*

Crop	Treatment																	
	Fresh compost			Piled compost			Stable manure			Mineral fertilizer			Non-fertilized		
	Soil	Crop	C/S[c]	Soil	Crop	C/S[c]	Soil	Crop	C/S[c]	Soil	Crop	C/S[c]	Soil	Crop	C/S[c]
	(μg/kg, dry wt)			(μg/kg, dry wt)			(μg/kg, dry wt)			(μg/kg, dry wt)			(μg/kg, dry wt)		
Horseradish															
root center	537	35.9	0.07	258	16.4	0.06	109.2	14.6	0.13	74.4	17.0	0.23	77.2	15.7	0.20
root skin	537	86.4	0.16	258	71.7	0.28	109.2	51.6	0.47	74.4	57.8	0.78	77.2	42.9	0.56
Red radish															
roots	482	70.4	0.15	221	55.8	0.25	150.2	37.9	0.25	66.3	19.1	0.29	83.9	19.9	0.23
Carrots[b]	85	0.11	0.0013												
Carrots[b]	130	0.16	0.0012												
Carrots[b]	185	0.08	0.004												

[a] PNAs include: fluoranthene, 3,4-benzofluoranthene, 3,4-benzpyrene, 1,12-benzperylene, 11,12-benzfluoranthene, Indeno(1,2,3-cd)pyrene (Borneff *et al.* 1973).
[b] For carrots only 3,4-benzpyrene monitored (Siegfried 1975).
[c] C/S = Crop/Soil ratio.

Table XXVII. *Effect of benz(a)pyrene on algal cell size and crop yield* (Graf and Nowak 1966).

PNA	Algae (*Chlorella* sp.) Size ratio (μ) (Experimental/control)	Algae (*Scenedesmus*) Size ratio (μ) (Experimental/control)	Algae (*Ankistradesmus*) Size ratio (μ) (Experimental/control)	Summer rye kernels Yield ratio (g) (Experimental/control)
[illegible]oranthene	1.08	1.20	1.21	0.28
1,21-Benzperylene	1.00	1.20	1.26	1.16
3,4-Benzfluoranthene	1.05	3.71	1.47	0.39
Indeno(1,2,3-cd)pyrene	1.11	1.14	1.32	1.63
1,2-Benzanthracene	1.16	1.19	0.97	1.08
3,4-Benzpyrene	1.19	2.07	1.16	1.35

Table XXVIII. *Effect of 3,4-benzfluoranthene in soils with wheat and barley* (Wagner and Wagner-Hering 1971).

3,4-Benzfluoranthene (μg/kg, dry wt) in soil	Plant				
	Wheat		Crop	Barley	
	(Yield, dry wt-g)	Concentration (μg/kg, dry wt)	Soil	(yield, dry wt-g) Root	Straw
Control (2.0)	20.8	100	50	10.4	36.8
130	21.3	237	1.83		
1300	20.8	223	0.18		
Control (2.0)	44.9	119	59.4		
3100	38.5	273	0.087		
6300	39.3	483	0.077		
9400				16.9	33.5
19000				12.4	34.3

The 'normal' presence of PNAs in plants and the stimulation of growth upon addition of PNAs to plants led Graf and Nowak (1966) and Graf (1965) to suggest that PNAs may be plant growth promoters (auxins) or their precursors.

While PNAs act to stimulate plant growth, they may not accumulate in the plant. Graf (1965) observed that B(a)P, supplied to tobacco through the roots, did not increase in concentration in the plant relative to the dry weight as compared to control plants. Thus, the B(a)P supplied to the plants is consumed during growing, with no net accumulation in the plant.

Tumor-like growth has also been reported for other plants. Ishio *et al.* (1972) reported neoplastic growth on marine algae. Mushrooms have also exhibited cancer-like growth in the presence of PNAs (NAS 1972).

Other researchers (Wagner and Wagner-Hering 1971) actually obtained growth depression and retardation with PNAs and higher plants. 3,4-Benzfluoranthanthene at 6200 μg/kg effected a reduced stem length of wheat (78 vs. 71 cm). Table XXVIII lists results of the effects of 3,4-benzfluoranthene on wheat and barley. While reduction in the yield of wheat is small, even at high 3,4-benzfluoranthene concentrations, there was an apparent uptake of the PNA which was related to the soil concentration. Apparently, wheat may accumulate 3,4-benzfluoranthene by a factor of five and not show significant yield reductions. At higher soil concentrations, 3,4-benzfluoranthene reduces root weight of barley plants by almost 50%, while reduction in straw yield is minimal. A selective effect of the PNA in retarding plant parts is suggested here.

c) Plant biosynthesis of PNAs

There is strong evidence for plant biosynthesis of PNAs. Borneff *et al.* (1968 a) demonstrated the biosynthesis of seven PNAs by algal cells using ^{14}C acetate as a sole carbon source. Results are presented in Table XXIX. The PNA concentrations are typical of background levels in plants. Graf and Diehl (1966) demonstrated an apparent synthesis of B(a)P by growing seeds of rye, lentils, wheat and hyacinths. Table XXX summarizes the results. These studies were conducted under controlled conditions to prevent the introduction of exogenous PNAs.

Table XXIX. *PNAs content in algae with ^{14}C-acetate as sole carbon source* (Borneff *et al.* 1968 b).

PNA	Concentration (μg/kg, dry wt)
Fluoranthene	54.62
Benz(a)anthracene	5.73
Benzo(b)fluoranthene	3.70
Benz(a)pyrene	0.70
Benzo(ghi)perylene	2.03
[illegible]nzo(k)fluoranthene	1.32
Indeno(1,2,3-cd)pyrene	1.50

Table XXX. *Benz(a)pyrene levels in higher plant seeds and seedlings grown hydroponically* (Graf and Diehl 1966).

Crop (seeds)	Concentration (μg/kg, dry wt)	Crop (seedlings)	Concentration (μg/kg, dry wt)	Seedlings/ seed ratio
Rye kernels	2.0	rye seedlings	18.0	9
Rye kernels	0.5	rye seedlings	38.0	76
Lentils	0.1	lentil seedlings	24.0	240
Wheat kernels	0.5	wheat seedlings	8.0	16
Hyacinth bulbs	3.0	hyacinths	10.0	3

Table XXXI. *PNA levels in young and old leaves of higher plants (μg/kg, dry wt)* (Graf and Diehl 1966).

PNA	Plant								
	Beech leaf			Oak leaf			Tobacco leaf		
	Green	Yellow	Y/G[a]	Green	Yellow	Y/G[a]	Green	Yellow	Y/G[a]
Fluoranthene	310	1200	4.0	126	666	5.3	376	626	1.7
Benzo(b)fluoranthene	62	374	6.0	62	292	4.7	32	126	3.9
Indeno(1,2,3-cd)pyrene	38	234	6.0	26	150	5.8	18	38	2.1
Benz(a)anthracene	26	166	6.4	18	100	5.6	12	44	3.7
Benzo(ghi)perylene	38	142	3.7	16	74	4.6	18	44	2.4
Benz(a)pyrene	16	66	4.1	8	42	5.3	12	38	3.2
Average			5.0			5.2			2.8

[a]Y/G = Yellow/Green ratio.

It was also reported by Graf and Diehl (1966) that the content of beech, oak, and tobacco leaves increased in PNA content as they mature from green to yellow (Table XXXI). It is interesting that all PNAs increase by about the same factor in tree leaves (5-fold) and in tobacco (3-fold) with aging.

Biosynthesis of PNAs has also been investigated with respect to bacterial synthesis (Brisou 1969). Very small (trace) quantities of B(a)P were observed with a variety of substrates. The rate of appearance of 3,4-benzpyrene in marine phytoplankton was investigated by Niaussat *et al.* (1969). Presence of B(a)P was demonstrated as due to the bacteria.

However, careful investigations with higher plants indicate that the biosynthesis scheme is still questionable. Grimmer and Duvel (1970) demonstrated that absence (0 μg/kg) of benz(e)pyrene, perylene, anthanthrene, benzo(ghi)perylene, dibenz(a,h)anthracene, and coronene in higher plants in growth chambers with filtered air. These PNAs were present in low concentrations in duplicate plants grown under greenhouse conditions. Results are summarized in Table XXXII. The soils and concentration of PNAs in soils used for those experiments were not discussed.

d) Phytotoxic effects of PNAs

The only phytotoxic effects reported for PNAs include reduced growth of wheat and barley (Wagner and Wagner-Hering 1971). This information is summarized in Table XXVIII. No effect was observed on rye, summer wheat, and green maize at 3,4-benzpyrene and 3,4-benzfluoranthene (B(b)F) concentrations up to 1,200 μg/kg. Increasing soil B(b)fluoranthene concentration to 6,254 μg/kg reduced stem growth in summer wheat, but did not significantly affect rye plants. Dry leaf mass was slightly reduced in the case of plants with B(b)F, and total dry yield was reduced by 11% (36.5 to 32.5 g). Phytotoxic

Table XXXII. *PNA levels in higher plants grown in different environments (μg/kg)* (Grimmer and Duvel 1970).

PNA	Climate-controlled (results for all plants)	Greenhouse			
		Lettuce	Tobacco	Rye	Soybean
Benz(e)pyrene	0	4.2	2.5	3.4	4.3
Benz(a)pyrene	0	3.7	1.8	1.6	3.1
Perylene	0	0.4	0.25	0.9	0.3
Anthanthrene	0	0.2	0	0.1	trace
Benzo(ghi)perylene	0	2.5	1.1	0.9	1.5
Dibenz(a,h)anthracene	0	0.4	trace	0.1	0.1
Coronene	0 (0.1[a])	0.6	0.1	0.1	0.4

[a]0.1 μg/kg for soybean only.

Table XXXIII. *Distribution of radioactivity among products of metabolism of* ^{14}*C-benzene in the tea plant* (Durmishidze and Ugrekhelidze 1969).

Part of plant	Organic acids									^{14}C as % of total radioactivity of the fraction amino acids							
	fumaric	succinic	malonic	malic	citric	glycollic	lactic	mandelic	dry residue[a]	leucine	valine	methionine	threonine	alanine	tyrosine	glycine	glutamic
Assimilation of benzene through the roots																	
Young roots		15.6	50	11.1					21.7	13	32	11.5	17.5			26	
Year-old roots	20	20	27	33						21.7	43.3	26					30
3-year roots	23	24.5	26.2	26.3						17.5	38.5		14				
Stem	88	12								18	24	20	14			2	22
Year-old shoots	64		10.5	25.5						17.1	22.2		23			14.2	8.5
Assimilation of benzene through the stem																	
Leaves	12.5		35		52.5					11.7	8	24		18.3	38		
Year-old shoots	30	70								7	28	21	7	3.5	33.5		
Stem above injection point	27	28.7	7.8			1.5	1.3	33.7		7	9.3	11.7	4.3	11.7	56		
Stem at injection point	7.1	51.4	21.4				3.4	16.7			9.4	28			62.6		
3-year roots	44	47.2	8.8							35	12.5	52.5					
Young roots	7.7	28.7	60								50	42.5	7.5				

[a] Dry residue from extraction with 80% ethanol.

effects are apparently not severe in these higher plants (wheat and barley) up to B(a)P and B(b)F soil concentrations of 18,000 μg/kg, even though it appears that B(b)F is bioaccumulated with the amount of uptake related to soil B(b)F concentration.

e) Plant metabolism of PNAs

Plants appear to be able to metabolize the benzene ring. Durmishidze and Ugrekhelidze (1969) demonstrated the cleavage of the carbon atom into organic acids and amino acids. Radioactive carbon was translocated from roots upward and from the stem downward and upward through the plant.

The first stable products of benzene metabolism by tea plants appear to be organic acids. These acids accumulate in the plant part where benzene was introduced (roots and stems).

A radioactivity balance indicated that radioactivity excreted as $^{14}CO_2$ (plants were kept in dark) during the experiment of 72 hr amounted to 3% for root application of benzene and 2% for stem application.

A proposed pathway for benzene degradation in plants was postulated:

benzene → phenol → pyrocatechol → *o*-benzoquinone → muconic acid

Table XXXIII presents the results for organic acid and amino acid distribution for benzene assimilated through roots and through the stem.

Durmishidze *et al.* (1973) studied the assimilation and conversion of labeled 3,4-benzpyrene-1,2-^{14}C with sterile corn and bean plants. The experiments were conducted on 14-day-old corn seedlings (*Zea mays*) and beans (*Phaseolus vulgaris*) cultivated under sterile conditions in a known nutrient medium. 3,4-Benzpyrene was introduced either through the roots or though the leaves. Results of the experiment, indicating the distribution of radioactivity in plant metabolism products are presented in Tables XXXIV and XXXV. Low molecular weight substances include organic acids, amino acids, and sugars. The dry residue not soluble in 80% ethanol represents the complex biopolymers.

The results show that higher plants are capable of metabolizing B(a)P when it is introduced to the roots or to the leaves. The quantity of unmetabolized B(a)P appeared to be a function of the length of time of the experiment. The largest fraction of radio-labelled carbon is associated with the low molecular weight substances, primarily organic acids. These are likely to be the primary products of biological degradation of B(a)P.

Durmishidze *et al.* (1974) extended their research on B(a)P metabolism to several additional plants including alfalfa (*Medicago sativa*), rye grass (*Lolium multiflorum*), chick-pea (*Cicer orientinum*), cucumbers (*Cucumis sativus*), pumpkin (*Cucurbita*), orchard grass (*Dactylis glome rata*), and vetch (*Vicia faba*). Results were similar to those obtained for corn and bean plants. Organic acids were most radioactive and were concentrated at the site of assimilatio[illegible] For [illegible]ssimilation by roots, organic acid radioactivity ranged from 5.4 to 5[illegible] of

Table XXXIV. *Assimilation of 3,4-benzpyrene-1,2-^{14}C by sterile seedlings of corn and beans (assimilation from roots, exposure 92 hr, temperature 18° to 22°C, in darkness)* (Durmishidze *et al.* 1973).

Plant	Plant organ	Radioactivity, thousand dpm/min on 1 g				
		Fraction of biopolymers	Fraction of low molecular wt substances + BP[a]	Fraction of organic acids	Fraction of amino acids	$^{14}CO_2$
Corn	roots	0.137	144.4	95.1	6	0.1
	leaves	0.364	8.95	4.2	1.15	–
Beans	roots	0.2	200.2	131.3	8.7	0.03
	leaves	0.11	7.1	3.25	1.1	–

[a]BP = 3,4-benzpyrene-1,2-^{14}C.

Table XXXV. *Assimilation of 3,4-benzpyrene-1,2-^{14}C by sterile seedlings of beans (assimilation from leaves, exposure 224 hr, temperature 19° to 22°C in darkness)* (Durmishidze *et al.* 1973).

Plant	Radioactivity, thousand dpm/min on 1 g				
	Fraction of biopolymers	Fraction of low molecular wt substances	Fraction of organic acids	Fraction of amino acids	$^{14}CO_2$
Beans (leaves and roots)	0.13	28.7	18.1	1.9	0.2

the total radioactivity of the root biomass. For assimilation by leaves the range was from 2.1 to 62.2% of the total radioactivity of the leaf biomass. Radioactivity was also incorporated into amino acids (up to 18% of total radioactivity) and $^{14}CO_2$ (up to 9%). The amount of 1,2-^{14}C-B(a)P metabolized ranged from 2 to 18% of the B(a)P assimilated by the plants.

VII. Conclusions

Polynuclear aromatic (PNA) compounds are a class of organics including hydrocarbon and heterocyclic species. Toxicity, metabolic and environmental fate, and environmental control of PNAs are topics of intense current study. Individual PNA compounds and isomers vary widely in their susceptibility to biodegradation; however, a consistent trend of decreasing biodegradation with increasing ring number is apparent. As shown, PNAs do decompose in soil systems, probably more rapidly than in any other waste management alternative or receiver systems involving biological activity. Research is needed to establish conclusively rates of decomposition and soil levels above which application of PNA constituents adversely affects the food chain. Thus utilization of a soil assimilative capacity concept will allow treatment of PNA compounds in an environmentally acceptable and cost effective manner. Research must be initiated to study enhancement factors that increase degradation rates of PNAs, especially those with more than three rings. Such research would not only add to present knowledge of PNA decomposition pathways by soil microorganisms under environmental conditions, but may also substantially increase the soil assimilative capacity and provide land application as an alternative technology that may be the most economical for safe and acceptable disposal of PNA wastes.

Based on the information presented, it appears that with bacterial seeding or in situ acclimation of a land application site, a substantial degradation rate could be achieved for the PNA class of compounds.

Of all degradation pathways considered, including volatilization and microbial degradation, the latter mechanism appears to be the most important in the environment.

Furthermore, natural regulation systems in the soil-plant cycle appear to keep plant uptake and biomagnification quite low in comparison to alternative stream receiver systems.

Storage and land-filling of PNA wastes are not ultimate solutions but simply postpone the problem of disposal; however, PNAs may be diluted in soil below threshold levels that are nontoxic and not a hazard to either food chain, water supplies, or agricultural productivity.

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