

**“MUSSEL WATCH” AND CHEMICAL CONTAMINATION OF THE COASTS BY
POLYCYCLIC AROMATIC HYDROCARBONS***

XA9951933

FARRINGTON, J. W.
Woods Hole Oceanographic Institution
360 Woods Hole Road - MS#31
Woods Hole, Massachusetts 02543-1541
U. S. A.

Abstract

Polycyclic aromatic hydrocarbons (PAH) enter the coastal marine environment from three general categories of sources; pyrogenic, petrogenic (or petroleum), and natural diagenesis.

PAH from different sources appear to have differential biological availability related to how the PAH are sorbed, trapped, or chemically bound to particulate matter, including soot. Experience to date with bivalve sentinel organism, or "Mussel Watch", monitoring programs indicates that these programs can provide a reasonable general assessment of the status and trends of biologically available PAH in coastal ecosystems. As fossil fuel use increases in developing countries, it is important that programs such as the International Mussel Watch Program provide assessments of the status and trends of PAH contamination of coastal ecosystems of these countries.

1. INTRODUCTION

Modern societies have deliberately and inadvertently discharged or released chemicals of environmental concern to the coastal ocean for decades. The serious nature of several of the ensuing problems identified in the 1960s and early 1970s demonstrated the need for an organized and systematic approach to assessing the status and trends of contamination of coastal and estuarine ecosystems by selected chemicals of major concern. Surveys in the 1960s and early 1970s involving sampling and analysis of various components of coastal and estuarine ecosystems led to the conclusion that much could be learned about spatial and temporal trends by sampling and analyzing carefully chosen populations of bivalves. Writing in 1975, Professor Edward D. Goldberg of Scripps Institution of Oceanography, California, USA [1] called for a "Mussel Watch" Program of assessment of contamination of the world's coastal oceans by using the bivalve sentinel organism approach for monitoring of selected chemicals. Shortly thereafter a few national or regional programs, for example the U. S. EPA "Mussel Watch" Program, were implemented as prototype monitoring programs. Valuable, multi-year experience was gained with this type of approach to coastal and estuarine monitoring and several important lessons were learned in these efforts, including the need for very close coupling of the monitoring program with ongoing biogeochemical and biological/ecological effects research [2-13].

A special concern for coastal areas of developing countries led to the establishment of the International Mussel Watch Program to provide an initial survey of coastal areas of developing countries for selected chemical contaminants, initially chlorinated pesticides and chlorobiphenyls, and to provide a framework for operational monitoring programs in individual countries and regions [5,7-10]. I submit that progress has been slower than originally anticipated and a global survey within a few year period of time has not been achieved to date as originally envisioned [8-10]. My personal experience suggests that this is the result of higher priorities being assigned elsewhere within international environmental quality efforts and a scarcity of funding to meet all the needs for research and monitoring for global environmental concerns.

*Contribution Number 9866, Woods Hole Oceanographic Institution. Support for preparation of this paper provided by U. S. National Science Foundation Grant OCE-9708478.

Chlorinated pesticides and chlorobiphenyls were the chemicals chosen for the focus during the initial stages of the International Mussel Watch Program. There was continuing use of chlorinated pesticides in some developing countries and data for both chlorinated pesticides and chlorobiphenyls could be obtained with modest additional analytical effort because of similarities in chemical properties of the compounds [5,8-10]. I contend in this paper that there are significant reasons for using the *International Mussel Watch* approach to assess the status and trends of concentrations of bioavailable polycyclic aromatic hydrocarbons in coastal areas in addition to chlorinated pesticides and chlorobiphenyls. A brief review of our knowledge of PAH biogeochemistry in coastal ecosystems followed by a summary from the ongoing US NOAA Status and Trends Mussel Watch Program and result from Phase I of the International Mussel Watch Program are presented in support of this contention.

2. BIOGEOCHEMISTRY OF POLYCYCLIC AROMATIC HYDROCARBONS: SEDIMENTS AND BIVALVES

Polycyclic aromatic hydrocarbons (PAH) are among the chemicals of environmental concern for three main reasons. First, some of the individual PAH are prototocarcinogens, that is uptake by organisms and biochemical activation to carcinogens is of significant potential under some conditions found in nature [14,15]. Second, other PAH can have deleterious effects on marine organisms if taken up by these organisms to high concentration levels [16]. Third, modern human civilization's activities are mobilizing these compounds to enter the environment, including the coastal environment, at rates much higher than natural rates before modern civilization [14,17-20].

Major sources of PAH input to the environment are listed in table I. It is important to keep in mind that there are hundreds to thousands of individual PAH structures in some of the sources of inputs. Despite significant analytical chemistry progress in analysis of PAH during the past three decades, there are formidable challenges remaining for analyses of environmental burdens of PAH. The details of that story are not the subject of this paper, but analyses of PAH in environmental matrices should be recognized as a continuing analytical chemistry challenge. During the mid-1970s when PAH data were collected for sediments from coastal areas, parameters were noted that distinguished in a general way between pyrogenic (parent PAH predominated over alkylated PAH in a homologous series) and petrogenic sources (alkylated PAH predominated over the parent PAH in a homologous series)[17,18]. The PAH composition of sediments generally indicated a pyrogenic origin from either, or both, natural fires and combustion of fuels by human activities [17,18]. PAH with a petrogenic source composition were found only in the most heavily industrialized harbor sediments or at oil spill sites, and often they were mixed with PAH with a pyrogenic source composition [17,18]. This has been confirmed several times during the past fifteen years [14,19,20]]. Use of ratios of selected isomer pairs sometimes discriminates further between combustion sources [21,22]. More recently, the ratios of stable isotopes of carbon and radioactive carbon content of individual PAH have been added as powerful parameters available for apportioning sources of the mixture of PAH present in various types of samples [23,24].

TABLE I. MAJOR SOURCES OF PAH INPUTS TO THE ENVIRONMENT.

| Pyrogenic Input. | Petroleum |
|---|---|
| Combustion of Fossil Fuels. | Oil seeps, Oil Spills, Chronic Oil releases |
| Transportation. | |
| Exhaust, Used lubricating oil | |
| Home heating and cooking | Automobile and Truck Tires |
| Electric power generation | |
| Industrial uses. | Early Diagenesis of Organic Matter |
| Forest and Grass Fires | |
| Home cooking and heating using wood, dung | |
| Creosote, Tar, Asphalt | |

Samples of mussels or oysters were collected at approximately 100 stations around the U. S. between 1976 and 1978 as part of the USEPA funded "Mussel Watch" [2-4], a prototype for the current US NOAA Status and Trends Program [25]. Bivalves from approximately fifty sites in the USEPA "Mussel Watch" Program were analyzed for PAH by quantitative GCMS by our group in Woods Hole. Bivalves sampled near urban harbor sites, for example New York and Boston, had elevated concentrations compared to samples from more remote locations such as the coast of Maine [4,26]. This was not a major surprise given the data for elevated PAH in sediments sampled near urban harbor areas [17-20]. The surprise came in the way of the qualitative mixture of PAH present; more petrogenic in origin than the PAH mixture found in sediments [4,26]. Bivalves in more remote locations with lower concentrations had primarily a pyrogenic source signature in accord with sediment PAH in remote locations [4,26]. We hypothesized that the pyrogenic PAH were more tightly bound to particles from combustion processes and thus were less bioavailable than petrogenic PAH which enter the coastal environment in various forms and were less tightly bound to particles and also dissolved or accommodated in water [4,26]. This highlighted the need to improve our understanding of the physical chemistry of the PAH in the environment and to understand how this relates to bioavailability of PAH.

At about the same time as our research led us to this hypothesis, Readman, Mantoura and others in Plymouth at the U. K. were researching and publishing results about PAH biogeochemistry of PAH in the Tamar Estuary, U. K. [27]. Their results, those of Prahl and Carpenter [28], Socha and Carpenter [29], Broman and co-workers [30], and more recent Ph. D. thesis research results of Susan McGroddy [31,32] Keith Maruya [33,34] Christopher Reddy [35] and Orjan Gustaffson [36,37], among several other research efforts, have contributed substantially to our present understanding of the physical-chemical form of PAH and relationships to bioavailability. Figure 1 is a simplified cartoon view of major physical chemical forms of PAH. The importance of binding to soot (bottom right example in figure 1.) has been discussed in theoretical terms and used to explain aspects of field observations of pore water-particle partitioning in sediments [36,37].

This improved understanding of the biogeochemistry of PAH in coastal ecosystems informs, or should inform, policies for regulating and reducing inputs of PAH, and to guide restoration and cleanup efforts in some heavily contaminated areas. Use of fossil fuels in developed countries continues to increase, albeit slower than before, as indicated by assessments and estimates of carbon emissions [38]. There are policies in place, such as recycling used motor oil, which should result in reduced release to the environment of amounts of PAH/unit fuel used. Have these policies been effective in reducing environmental burdens of PAH? What is the status of bioavailable PAH concentrations in coastal ecosystems?

3. PAH IN COASTAL ECOSYSTEMS: PRESENT AND FUTURE STATUS AND TRENDS

The U.S. NOAA Status and Trends Program provides high quality monitoring data that yields a portion of the answer for the U. S. Coast. Bivalves from over 100 sites have been sampled and analyzed annually between 1986 and 1995 for the suite of PAH [25,39]. Concentrations of PAH in bivalves have about the same distribution that we noted in our prototype efforts of the late 1970s; elevated concentrations are found near urban harbor areas and lower concentrations are found in remote locations [25,39]. The main issue relevant to this presentation is the temporal trend. A summary of the observed temporal trends for organic chemicals of environmental concern analyzed in the program is presented in table II [39]. For PAH, three sites had trends of increasing concentration, three sites had trends of decreasing concentrations and for the remaining 180 sites the concentrations remained the same. This contrasts with several other suites of organic chemicals of environmental concern for which at most only one site had an increasing trend and many more sites had decreasing trends (Table II). There is good news in these data since the continued increased use of fossil fuels has not resulted in trends of increasing concentrations of PAH. For urban harbor areas with high concentrations of PAH in bivalve tissues, the continued elevated concentrations may be sustained by inputs to the surrounding ecosystem from sediments containing past inputs of PAH. [31-34].

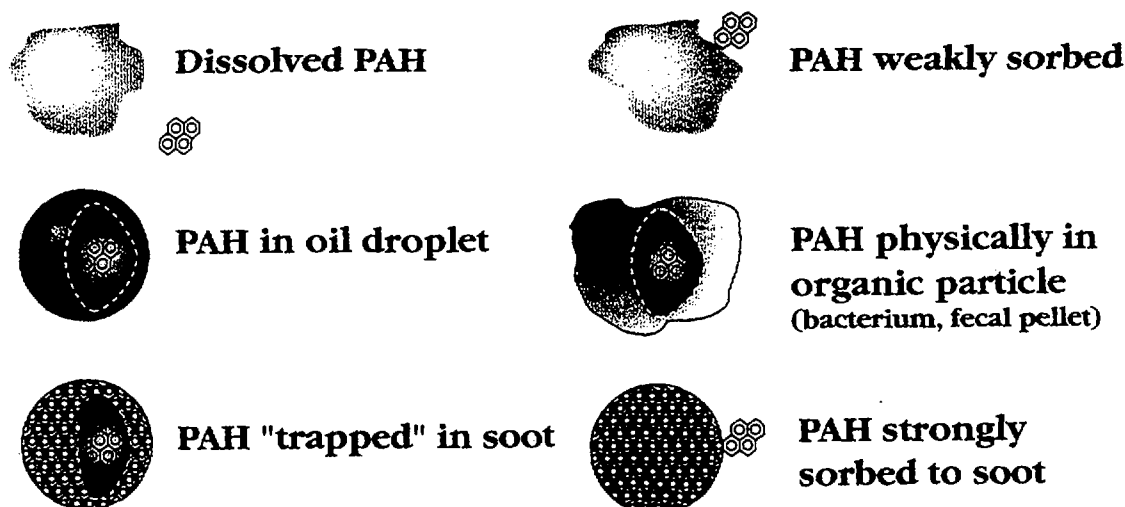


FIG. 1. Some Physical-Chemical Forms of PAH in the Environment: Example of Pyrene Interaction with Particulate Organic Matter, Oil Droplet and Soot. Modified from Reference [27].

TABLE II. U. S. NOAA STATUS AND TRENDS MUSSEL WATCH DATA: NUMBERS OF SITES WITH INCREASING, DECREASING, OR NO TREND IN CONCENTRATIONS OF EACH CHEMICAL. 1986-1995[39].

| Chemical | Increase | Decrease | No Trend |
|-----------------------|----------|----------|----------|
| * Σ Chlordane | 1 | 81 | 104 |
| * Σ DDT | 1 | 38 | 147 |
| * Σ Dieldrin | 1 | 32 | 153 |
| * Σ PCB | 1 | 37 | 148 |
| Σ PAH | 3 | 3 | 180 |
| * Σ Butyl Tins | 0 | 18 | 168 |

*Chemicals with decreasing trends in concentrations in mussels and oysters.

These data and interpretations for the U. S. coast are of concern when combined with limited data available for PAH in samples from coastal areas of developing countries. During the first phase of International Mussel Watch in the Central, South America, and Caribbean regions, the emphasis was on analyses of chlorinated pesticides and selected PCB congeners [8, 40]. In addition, Sericano et al [40] analyzed many of the samples for the same suite of PAH analyzed for the NOAA Status and Trends Program. The range of concentrations of PAH are similar to those found in the U. S. National Status and Trends Program, with fewer samples of the total having elevated concentrations. Elevated concentrations are found near urban areas, and the composition of the PAH indicate a mixture of petrogenic and pyrogenic sources [40].

These measurements are one point-in-time - a survey. A good start, but insufficient if we consider the known and projected fossil fuel use indicated by carbon emissions trends for developing countries [38]. This will lead to an increase in by-product combustion source PAH and there will be increased mobilization of petroleum PAH. Leakage will occur and it is likely that environmental burdens of PAH will increase in coastal areas. The extent of the increase will depend upon how lessons from the developed countries about curtailing sloppy use of fossil fuels and reducing inputs of PAH are adopted and adapted to policy and management decisions in developing countries.

I am concerned that there are no systematic collections of PAH data for coastal areas that will provide assessments of trends over time and space, and provide feedback for effective management of the inputs of PAH to coastal ecosystems in developing countries. The International Mussel Watch Program and follow-on or associated regional programs offer a means to track trends in bioavailable

PAH concentrations. I do not advocate a focus on PAH to the exclusion of other chemicals of environmental concern. Coupled with emerging and powerful biological effects measurements, assessments of the status and trends of coastal ecosystem burdens of chemicals of environmental concern can provide for a powerful monitoring methodology that should be applied in coastal areas worldwide.

References

- [1] GOLDBERG, E.D., The Mussel Watch: a first step in global marine monitoring. *Marine Pollut. Bull.* **6**(1975) 111.
- [2] GOLDBERG, E.D., et al, The Mussel Watch. *Environ. Conserv.* **5**(1978) 101-125.
- [3] GOLDBERG, E.D., et al, U. S. Mussel Watch: 1977-1978 results on trace metals and radionuclides. *Estuarine, Coastal and Shelf Sci.* **16**(1983) 69-93.
- [4] FARRINGTON, J. W., et al, U. S. Mussel Watch 1976-1978: An overview of the trace metal, DDE, PCB, hydrocarbon and artificial radionuclide data. *Environ. Sci. Technol.* **17**(1983) 490-496.
- [5] GOLDBERG, E.D. (Ed.), The International Mussel Watch. (Report of a Meeting in Barcelona, Spain, December, 1978.), National Academy of Sciences Publications Office, Washington D. C. (1980).
- [6] PHILIPS, D.J.H., Quantitative Biological Indicators. Their Use to Monitor Trace Metal and Organochlorine Pollution. Applied Science, London (1980).
- [7] SIVALINGHAM, P. M. Chemical Changes in the Coastal Zone. *Marine Pollut. Bull.* **15** (1984),86.
- [8] FARRINGTON, J.W., TRIPP, B.W.(Eds.), International Mussel Watch, Initial Implementation Phase, Final Report. UNESCO-IOC, UNEP, U. S. NOAA, NOAA Technical Memorandum NOS ORCA 95, (1995).
- [9] TRIPP, B.W. et al., International Mussel Watch: The initial implementation phase. *Marine Pollut. Bull.* **24**,(1992), 371-373.
- [10] UNESCO-IOC. International Mussel Watch: A Global Assessment of Environmental Levels of Chemical Contaminants. UNESCO-IOC, Paris, France (1992).
- [11] Report of the International Mussel Watch Organizational Meeting, Asian Pacific Phase. January 20-22, 1993. The United Countries University, Tokyo, Japan, (1993).
- [12] UNEP. Contaminant Monitoring Programmes using Marine Organisms: Quality Assurance and Good Laboratory Practice. *Marine Pollution Studies No. 57*. United Countries Environment Programme. (1990)
- [13] CANTILLO, A. Y. Mussel Watch Worldwide Literature Survey-1991. NOAA Technical Memorandum NOS ORCA 63, National Oceanic and Atmospheric Administration, Rockville, MD, USA. (1991)
- [14] National Research Council. Polycyclic Aromatic Hydrocarbons: Evaluation of Sources and Effects. National Academy of Sciences Press, Washington, D. C. (1983).
- [15] DAWE, C. AND STEGEMAN, J. (Eds.) Symposium on Chemically Contaminated Aquatic Food Resources and Human Cancer Risk. *Environ. Health Perspectives* **90** (1991), 3-149.
- [16] National Research Council. "Oil in the Sea". National Academy Press, Washington, D. C. (1985).
- [17] YOUNGBLOOD, W. W., BLUMER, M. Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. *Geochim. Cosmochim. Acta.* **39**(1975) 1303-1314.
- [18] LAFLAMME, R. E., HITES, R.A. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochim. Cosmochim. Acta.* **42**(1978) 289-303.
- [19] WAKEHAM, S.G., FARRINGTON, J.W.. Hydrocarbons in contemporary aquatic sediments. Chapter 1. In Baker, R. A. (Ed.). *Contaminants and Sediments*. Vol. 1. Sciences Publishers, Inc., Ann Arbor, Michigan (1980).
- [20] GSCHWEND, P. M., HITES, R.A., et al, Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. *Geochim. Cosmochim. Acta.* **45**(1981) 2359-2367.
- [21] BENNER, B. A. et al, Distinguishing the contribution of residential wood combustion and

- mobile source emissions using relative concentrations of dimethyl phenanthrene isomers. *Environ. Sci. Technol.* **29**(1995) 2382-2389.
- [22] BUDZINSKI, H. et al., Differentiation of contamination sources in recent sediments through PAH distributions: an overview. *Organic Geochemistry; developments and Applications to energy, climate, environment, and human history* [GRIMALT, J., DORRENSORRO, C., Eds.] 616-618 (1995).
- [23] O'MALLEY, V.P. et al, Determination of $^{13}\text{C}/^{12}\text{C}$ ratios of individual PAH from environmental samples: can PAH sources be apportioned? *Org. Geochem.* **21**(1994) 809-822.
- [24] LICHTFOUSE, E., et al, Ancient polycyclic aromatic hydrocarbons in modern soils. ^{13}C , ^{14}C , and biomarker evidence. *Org. Geochem.* **26** (1997) 353-359.
- [26] FARRINGTON, J.W. et al., Hydrocarbons, polychlorinated biphenyls, and DDE in mussels and oysters from the U. S. coast, 1976-1978 - The Mussel Watch. Technical report WHOI 82-42, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, U. S. A. (1982).
- [25] OCONNOR, T.P. recent trends in coastal environmental quality: results from the first five years of the NOAA Mussel Watch project. NOAA, U. S. Department of Commerce, Rockville. Maryland, U.S. (1992).
- [27] READMAN, J. W., et al, The Physico-chemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *Fresenius Z. Anal. Chem.* **319**(1984) 126-131.
- [28] PRAHL, F. G., et al, The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. *Geochim. Cosmochim. Acta* **43**(1979) 1959-1972.
- [29] SOCHA, S. B., CARPENTER, R. R. *Geochim. Cosmochim. Acta.* **51**(1987), 1273-1284.
- [30] BROMAN, D. et al, The importance of spheroidal carbonaceous particles (SCPs) for the distribution of particulate polycyclic aromatic hydrocarbons (PAHs) in an estuarine-like urban coastal water area. *Chemosphere* **21**(1990) 69-77.
- [31] MCGRODDY, S. E., FARRINGTON, J.W., Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environ. Sci. Technol.* **29**(1995), 1542-1550.
- [32] MCGRODDY, S. E., et al, Comparison of the *in situ* and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci. Technol.* **30**(1996)172-177.
- [33] MARUYA, K. A., et al, Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their porewaters. *Environ. Sci. and Technol.* **30**(1996) 2942-2947.
- [34] MARUYA, K. A., et al, The bioaccumulation of polynuclear aromatic hydrocarbons by benthic invertebrates in an intertidal marsh. *Environ. Toxicol. Chem.* **16** (1997) 1087-1097.
- [35] REDDY, C. M. et al, Environmental chemistry of bibenothiazoles derived from rubber. *Environ. Sci. Technol.* **31**(1997), 2847-2853.
- [36] GUSTAFSSON, O., et al, Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **31**(1997), 203-209.
- [37] GUSTAFSSON, O. and Gschwend, P. M. Soot as a strong partitioning medium for polycyclic aromatic hydrocarbons in aquatic systems. Chapter 4 in *Molecular Markers in Environmental Geochemistry* (Proc. Symp.) ACS Symposium Series 671(EGANHOUSE, R. P. ,Ed.), American Chemical Society, Washington, D. C. (1997). 365-381.
- [38] COONEY, C. N., Countries seek " Fair" geenhouse gas treaty in Kyoto. *Environ. Sci. Technol.* **31**(1998) 517A .
- [39] NOAA (on-line). "Chemical Contaminants in Oysters and Mussels" O"CONNOR, T., NOAA's State of the Coast Report. <http://state-of-coast.noaa.gov/bulletins/html/ccom_05/ccom.html >
- [40] SERICANO, J. L., et al, Trace organic contaminants in the Americas: an overview of the US National Status and Trends and the International Mussel Watch Programmes. *Marine Pollut. Bull.* **31**(1995) 214-225.