Kazuichi Hayakawa *Editor*

Polycyclic Aromatic Hydrocarbons

Environmental Behavior and Toxicity in East Asia

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Preface

At the beginning of the twenty-first century, atmospheric and marine environmental problems in Asia came to attract much global interest. The World Health Organization (WHO) reported that in 2012, an estimated 6.5 million deaths (11.6% of all global deaths) were associated with indoor and outdoor air pollution and some 3 million deaths a year were linked to exposure to air pollutants such as ambient fine particulates ($PM_{2.5}$).

Polycyclic aromatic hydrocarbons, or polynuclear aromatic hydrocarbons (PAHs), are produced through the incomplete combustion of organic matter (e.g., coal combustion, automobile engines, incinerators, smoking, cooking, biomass burning in forests, slash-and-burn agriculture, etc.). Through these processes, PAHs such as benzo[*a*]pyrene (BaP) and nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1-nitropyrene (1-NP) have become ubiquitous environmental organic pollutants. Several PAHs such as BaP are carcinogenic and mutagenic, and several NPAHs such as 1-NP and its further nitrated products are highly mutagenic. Large amounts of PAHs and NPAHs are concentrated in atmospheric $PM_{2.5}$, and so the inhalation of these particulates becomes especially hazardous.

PAHs and NPAHs are not restricted to the atmospheric environments. These pollutants reach the ground by rain/snow and finally flow through rivers into the sea, where there is also the direct atmospheric deposition into the sea. PAHs also occur naturally in oil, and oil spills cause serious large-scale marine pollution. Altogether, it is important to consider environmental pollution in Asia as a transboundary pollutant.

There have been several books concerning PAHs and their related compounds, but there is no book concerning PAH and NPAH contamination in the context of environmental pollution in Asia. This book begins with the fundamental chemistry and general behavior of these compounds as well as the analytical methods used in measuring their concentrations. Further discussion looks at the atmospheric and marine levels in Asian countries, the metabolic activation and toxicities, and the environmental standards and guidelines for PAHs and related compounds.

Kanazawa, Japan Kazuichi Hayakawa

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Abbreviation

AceNQ	Acenaphthoquinone
Ace	Acenaphthylene
1-AAP	*N*-Acetyl-1-aminopyrene
1-AP	1-Aminopyrene
Ant	Anthracene
1,4-AQ	1,4-Anthraquinone
9,10-AQ	9,10-Anthraquinone
9,10-AQ-d_8	9,10-Anthraquinone-octadeuterated
BaA	Benz[*a*]anthracene
7,12-BAQ	7,12-Benzanthraquinone
BbF	Benzo[*b*]fluoranthene
BkF	Benzo[*k*]fluoranthene
BgPe, BghiPe	Benzo[*ghi*]perylene
BaP	Benzo[*a*]pyrene
BeP-4,5-Q	Benzo[*e*]pyrene-4,5-quinone
BaP-d_{12}	Benzo[*a*]pyrene-dodecadeuterated
BaP-1,6-Q, BaP-3,6-Q, BaP-4,5-Q, BaP-6,12-Q, BaP-7,8-Q, BaP-7,10-Q, BaP-11,12-Q,	Benzo[*a*]pyrene-1,6-quinone, benzo[*a*]pyrene-3,6-quinone, benzo[*a*]pyrene-4,5-quinone, benzo[*a*]pyrene-6,12-quinone, benzo[*a*]pyrene-7,8-quinone, benzo[*a*]pyrene-7,10-quinone, benzo[*a*]pyrene-11,12-quinone
BcP-1,4-Q, BcP-5,6-Q	Benzo[*c*]phenanthrene-1,4-quinone, benzo[*c*]phenanthrene-5,6-quinone
BQ	1,4-Benzoquinone
BQ-d_4	1,4-Benzoquinone-quadrudeuterated
oxo-PAHs	Carbonyl polycyclic aromatic hydrocarbons
Chr	Chrysene
1,2-, 1,4-, 5,6-CQ	1,2-, 1,4-, 5,6-Chrysenequinone

5,6-CQ-d_{12}	5,6-Chrysenequinone-dodecadeuterated
DBA	Dibenz[*a,h*]anthracene
DBahA-5,6-Q	Dibenz[*a,h*]anthracene-5,6-quinone
DBajA-7,14-Q	Dibenz[*a,j*]anthracene-7,14-quinone
DiOH-1-NP	*Trans*-4,5-dihydro-4,5-dihydroxy-1-nitropyrene
2,5-, 2,6-DMBQ	2,5-, 2,6-Dimethylbenzoquinone
1,3-, 1,6-, 1,8-DNP	1,3-, 1,6-, 1,8-Dinitropyrene
Frt, Flu	Fluoranthene
Frt-2,3-Q	Fluoranthene-2,3-quinone
Fle	Fluorene
9-Fle	9-Fluorenone
FNF	3-Fluoro-7-nitrofluorene
OHPAH	Hydroxylated polycyclic aromatic hydrocarbon
OHNAAP	Hydroxy-*N*-acetyl-1-aminopyrene
2-, 3-, 4-OHBaA	2-, 3-, 4-Hydroxybenz[*a*]anthracene
3-OHBcP	3-Hydroxybenzo[*c*]phenanthrene
3-OHBaP	3-Hydroxybenzo[*a*]pyrene
3-OHFrt	3-Hydroxyfluoranthene
2-, 9-OHFle	2-, 9-Hydroxyfluorene
1-, 2-OHNap	1-, 2-Hydroxynaphthalene
2-OH-1,4-NQ	2-Hydroxy-1,4-naphthoquinone
OHNP	Hydroxy-1-nitropyrene
OHPAH	HydroxyPAH
2-, 3-, 4-, 9-OHPhe	2-, 3-, 4-, 9-Hydroxyphenanthrene
OHPyr	1-Hydroxypyrene
IDP	Indeno[1,2,3-*cd*]pyrene
2-MBQ	2-Methyl-1,4-benzoquinone
2-MNQ	2-Methyl-1,4-naphthoquinone
5,12-NapQ	5,12-Naphthacenequinone
Nap	Naphthalene
NaP-d_8	Naphthalene-pentadeuterated
1,2-, 1,4-NQ	1,2-, 1,4-Naphthoquinone
1,4-NQ-d_6	1,4-Naphthoquinone-hexadeuterated
5-NAc	5-Nitroacenaphthene
2-, 9-NA	2-, 9-Nitroanthracene
7NBaA	7-Nitrobenz[*a*]anthracene
6-NBaP	6-Nitrobenzo[*a*]pyrene
6-NC	6-Nitrochrysene
2-, 3-NFR	2-, 3-Nitrofluoranthene
2-NF	2-Nitrofluorene
1-, 3-NPer	1-, 3-Nitroperylene
4-, 9-NPh	4-, 9-Nitrophenanthrene
NPAH	Nitropolycyclic aromatic hydrocarbon
1-, 2, 4-NP	1-, 2, 4-Nitropyrene
2-NTP	2-Nitrotriphenylene

Phe	Phenanthrene
9,10-PQ	9,10-Phenanthrenequinone
9,10-PQ-d_{10}	9,10-Phenanthrenequinone-decadeuterated
9,10-Phe-diol	Phenanthrene-9,10-dihydrodiol
1,4-, 9,10-PQ	1,4-, 9,10-Phenanthrenequinone
Phe-d_{10}	Phenanthrene-decadeuterated
PAH	Polycyclic (polynuclear) aromatic hydrocarbon
PAHQ	Polycyclic aromatic hydrocarbon quinone
Pyr	Pyrene
1,6-, 1,8-, 4,5-PyrQ	1,6-, 1,8-, 4,5-Pyrenequinone
Pyr-d_{10}	Pyrene-decadeuterated
TMBQ	Tetramethylbenzoquinone

Part I

Fundamental Chemistry and General Characteristics

Chapter 1
Chemistry of Polycyclic Aromatic Hydrocarbons (PAHs), Nitropolycyclic Aromatic Hydrocarbons (NPAHs) and Other Oxidative Derivatives of PAHs

Kazuichi Hayakawa

Abstract Polycyclic aromatic hydrocarbons (PAHs) are composed of two or more fused aromatic (benzene) rings which contain only carbon and hydrogen. They are converted to derivatives including metabolites such as hydroxyl, quinoid, nitrated and halogenated PAHs. In order to understand their behaviours and toxicities, an understanding of the fundamental chemistry of PAHs and their derivatives is important. This chapter deals with their structure and properties, nomenclature, sources and toxicity.

Keywords Polycyclic aromatic hydrocarbon · Nitropolycyclic aromatic hydrocarbon · Hydroxypolycyclic aromatic hydrocarbon · Quinoid polycyclic aromatic hydrocarbon · Structure · Nomenclature

1.1 Introduction

Polycyclic aromatic hydrocarbons (or polynuclear aromatic hydrocarbons, PAHs) are composed of two or more fused aromatic (benzene) rings which contain only carbon and hydrogen. PAHs are thought to have been formed in tandem with new stars and exoplanets after the Big Bang and are still commonly observed in space. PAHs are also considered as possible starting compounds for the abiological synthesis of the earliest materials for life. PAHs are present in oil, tar and coal. They are also produced through the incomplete combustion of organic matter (e.g. coal combustions, automobile engines, incinerators, biomass burning in forest and slash-and-burn agriculture, smoking and cooking, etc.). Therefore, PAHs such as benzo[*a*]

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pyrene (BaP) and nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1-nitropyrene (1-NP) are ubiquitous environmental organic pollutants.

1.2 Structure, Nomenclature and Properties

PAHs observed in the environment are molecules having two to seven rings. Within this range, there are a large number of PAHs with different structures. Naphthalene ($C_{10}H_8$) is the smallest PAH with two aromatic rings, while coronene ($C_{24}H_{12}$) is the largest PAH and has six rings. The International Union of Pure and Applied Chemistry (IUPAC) has a recommended nomenclature for PAHs (Moss 1998). According to the IUPAC rules, the names of several common PAHs such as anthracene, phenanthrene, chrysene and pyrene form the basis for the nomenclature of other PAHs (Fig. 1.1). The names of common PAHs which are formed by the attachment of benzene rings are shown in Fig. 1.2. The important points of the IUPAC rules are described below:

1. Carbon atoms are numbered in a clockwise direction starting with the carbon atom that is not part of another ring and is in the most counterclockwise position of the uppermost ring or, if there is a choice, of the uppermost ring furthest to the right. Carbon atoms common to two or more rings are not numbered.

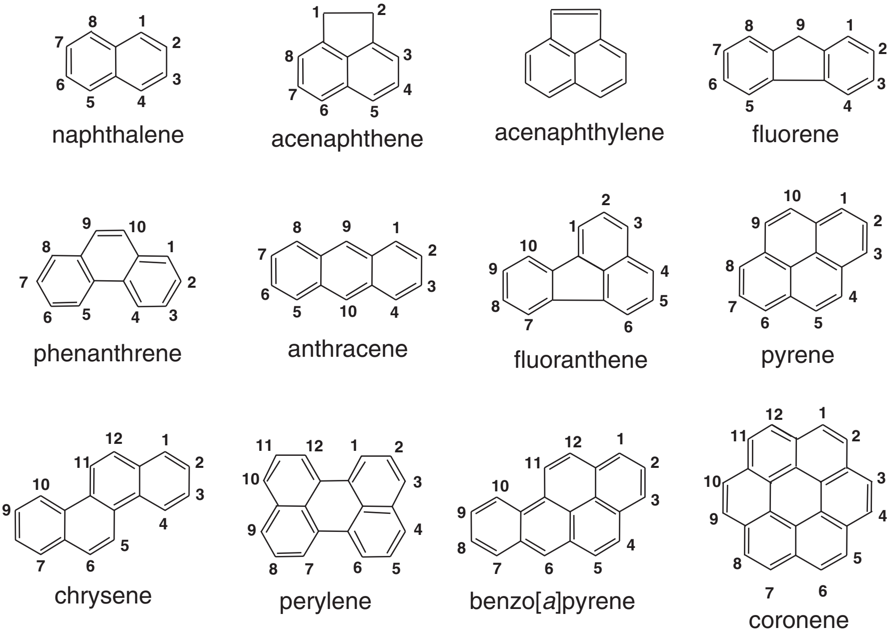

Fig. 1.1 Carbon numbering rules for fundamental PAHs

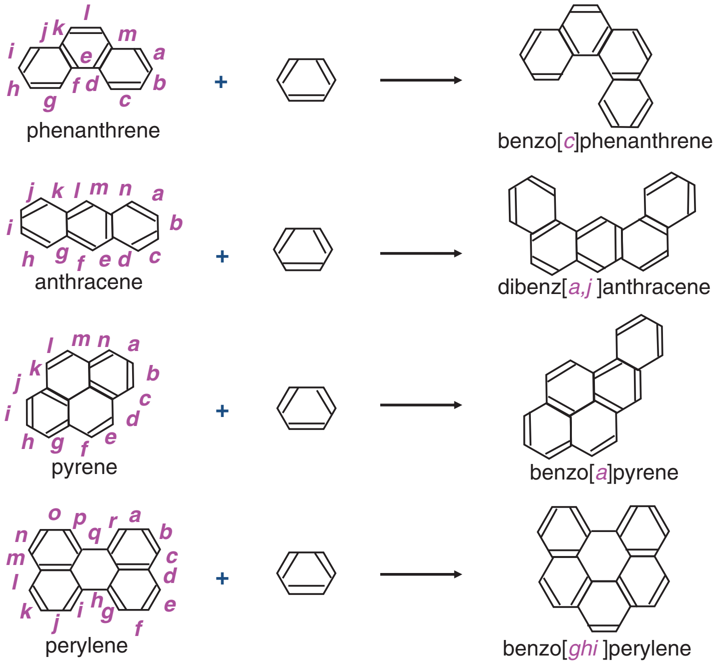

Fig. 1.2 Naming of PAHs attached with benzene rings

2. Ring faces, which are not common to two rings, are lettered in alphabetical order with the side between carbon atoms 1 and 2 designated "*a*". Alphabetical order is continued clockwise around the molecule.
3. Compounds (or isomers) formed by the addition of a benzene ring are named with numbers and letters enclosed in brackets [ ] but not in parentheses ( ). These are placed immediately after the name of the added component to describe where a substituent group is attached or where a ring is fused to the face of the molecule. Appropriate letters are used where a ring is fused to more than one face of the molecule.
4. The structural formulas used show aromatic rings as plain hexagons.

Nitro, hydroxy and quinoid derivatives of PAHs are formed through oxidation in the environment. Some hydroxy and quinoid PAHs are found in animal bodies as metabolites of polycyclic aromatic hydrocarbons (Burczynski and Penning 2000; Van de Wiele et al. 2005). The nomenclature rules for these PAH derivatives are shown in Fig. 1.3, and names of important NPAHs are shown in Fig. 1.4.

PAHs are neutral, hydrophobic nonpolar molecules. Physical and chemical characteristics, such as solubility in water, hydrophobicity and vapour pressure, vary with molecular weight (Table 1.1). These characteristics cause differences in redox potential, volatility, solubility, environmental/biological degradation resistance and toxicity. As an important characteristic of PAHs, fluorescent activity is used for the

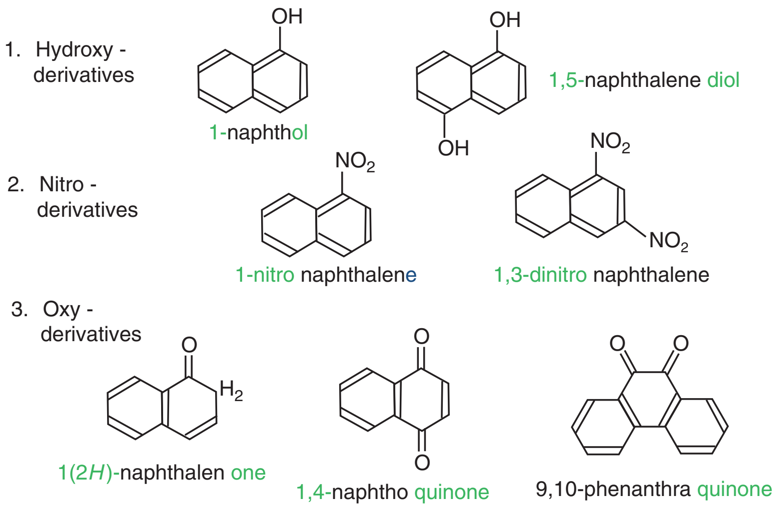

Fig. 1.3 Nomenclature for nitro, hydroxy and quinoid derivatives of PAHs

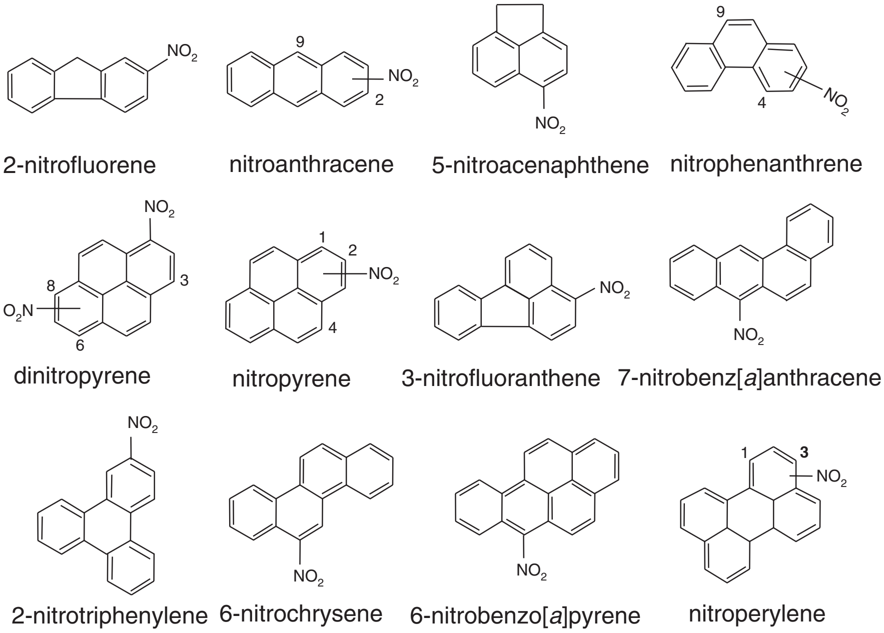

Fig. 1.4 Names of nitropolycyclic aromatic hydrocarbons

Table 1.1 Properties of PAHs

PAHs	Molecular mass (g/mol)	Vapor pressure (Pa at 25°C)[a]	Water solubility (mg/L)[b]	Henry's Law constant (Pa m^3/mol)[c]	Log K_{ow}[b]	Log K_{oc}[b]
Naphtharene, Nap	128	10.4	31.7	48.9[d]	3.4	3.1
Acenaphthlene, Ace	154	2.9×10^{-1}	3.93	15.7	4	1.4
Fluorene, Fle	166	9×10^{-2}	1.68–1.98	7.75	4.5	3.9
Phenanthrene, Phe	178	2×10^{-2}	1.2	3.981	4.5	4.2
Anthracene, Ant	178	1×10^{-3}	0.076	7.19	4.5	4.2
Fluoranthene, Flu	202	1.23×10^{-3}	0.2–0.26	0.659	5.2	4.6
Pyrene, Pyr	202	6×10^{-4}	0.0013	1.1	5.2	4.6
Benzo[*a*] anthracene, BaA	228	2.8×10^{-5}	0.01	0.248	5.9	5.3
Chysene, Chr	228	5.7×10^{-7}	0.0028	0.1064	5.9	5.3
Benzo[*b*] fluoranthene, BbF	252		0.012	1.236	6.6	5.7
Benzo[*k*] fluoranthene, BkF	252	5.2×10^{-8}	0.00076	0.111	6.1	5.7
Benz[*a*]pyrene, BaP	252	7×10^{-7}	0.0023	0.5	6.5	6.7
Dibenzo[*a,h*] anthracene, DBA	278	3.7×10^{-10}	0.0025	7.4×10^{-3}	6.5	6.5
Benzo[*ghi*] perylene, BghiPe	276		0.062	0.0146[d]	7.1	6.2
Indeo[*1,2,3-cd*] pyrene, IDP	276		2.6×10^{-7}	0.162	6.6	6.2

a) Saarnio et al. 2008; b) Feng et al. 2007; c) Baker and Eisenreidh 1990; d) Mackay et al. 1992

sensitive determination of PAHs, although several exceptions such as acenaphthylene exist. The structures of several NPAHs found in the atmosphere are shown in Fig. 1.2. Polarities of NPAHs are increased by the addition of nitro groups, but because of the strong electron withdrawing effect from the NO_2 group, NPAHs do not fluoresce and need to be converted to their amine analogues in order to have fluorescent activity (Murayama and Dasgupta 1996).

1.3 Sources

Both PAHs and NPAHs are formed through the incomplete combustion of organic matter and are directly emitted from diesel and gasoline engines, kerosene heaters, incinerators and other sources. These compounds are also found in cigarette smoke, food stuffs, waste water and sediment and are components of particulate matter (PM) in the atmosphere. The development of the economic and industrial activity from East Asia has been accompanied with a large increase in energy consumption (see Chap. 9). In particular, the primary energy consumption of China reached 12% of the total world consumption in 2014 (BP 2015). In East Asia, the main energy sources are oil in Japan and Korea, coal in China and both coal and natural gas in Russia. The burning of these fuels and biomass releases many pollutants, both gaseous and particulate, into the atmosphere. Recent heavy air pollution containing PM from China has been caused by the increase in the combustion of coal and petroleum. High concentrations of PM with a diameter of 2.5 μm or less ($PM_{2.5}$) in Beijing have been reported in January 2013 (Embassy of the United States, Beijing, China 2015). Similarly, high $PM_{2.5}$ levels have also been reported in India (Bisht et al. 2015; Bran and Srivastra 2017). These high levels of $PM_{2.5}$ containing PAHs and NPAHs in such densely populated areas are especially hazardous as they may cause respiratory, cardiac and lung diseases such as asthma and cancer (IARC 2013).

Crude oil is another source of PAHs. Oil spills from tankers and/or oil wells have resulted in the pollution of a number of marine areas (Dalton and Jin 2010; Gade and Alpers 1999). The Deepwater Horizon oil spill in the Gulf of Mexico occurred on April 22, 2010, and is the largest accidental oil spill in world history, and it estimated that about 7.0×10^5 m^3 of oil was released (Crone and Tolstoy 2010). The released oil and the dispersants used caused serious damage to marine organisms such as birds, coral, mussels and fish (Goodbody-Gringley et al. 2013; Haney et al. 2014; Stieglitz et al. 2016). Although the long-term effects of the oil on the fragile ecosystem remain unknown, the toxicity of oil is in part a function of the toxicity of PAHs.

1.4 4. Fundamental Toxicity

Many PAHs and NPAHs are carcinogenic and/or mutagenic. For example, the International Agency for Research on Cancer (IARC) has rated BaP under Group 1 (carcinogenic to humans), 1-NP in Group 2A (probably carcinogenic to humans) and several other PAHs and NPAHs in Group 2B (possibly carcinogenic to humans). Generally speaking, PAHs show indirect-acting mutagenicity (with the S9 mix) in the *Salmonella typhimurium* strains, but NPAHs show stronger direct-acting mutagenicity (without the S9 mix) in the same strains (see Chap. 18). Among these compounds, 1,3-, 1,6- and 1,8-dinitropyrenes (DNPs) have shown the strongest direct-acting mutagenicity (Arce and Morel 2013; Nakagawa et al. 1983). According to the IARC, 1,8-DNP is possibly carcinogenic to humans (IARC 2017).

In 2013, the World Health Organization (WHO) ranked $PM_{2.5}$ as Group 1 contaminants, because several PAHs and NPAHs, such as BaP and 1-NP, are carcinogenic (IARC 2017). Furthermore, metabolites of PAHs and NPAHs, such as hydroxylated and quinoid derivatives, have estrogenic/antiestrogenic or antiandrogenic activities (Kizu et al. 2000; Hirose et al. 2001; Hayakawa et al. 2007), and these oxidative metabolites can also produce reactive oxygen species (Kumagai et al. 2000; Motoyama et al. 2009). Therefore, a proper estimation of the human exposure to PAHs and NPAHs is important from the point of view of toxicity markers of $PM_{2.5}$. The detailed toxicities of PAHs and their derivatives are reviewed in Part VI.

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Chapter 2
PAHs and NPAHs in Airborne Particulate Matter: Initial Formation and Atmospheric Transformations

Edward Gou Nagato

Abstract In this chapter, the formation of early benzene and naphthalene rings is first discussed in the context of soot formation. While the hydrogen abstraction-acetylene addition (HACA) pathway is the most commonly accepted pathway, studies have shown that it is insufficient to account for the rapid formation of larger PAHs and soot, and so other mechanisms for PAH formation are discussed. Once the initial PAHs are formed, they can undergo further transformation, for example, forming nitrated (NPAHs) or oxygenated analogues. The formation of NPAHs can occur through three routes: formation through combustion processes (primary production), through the transformation of PAHs in the atmosphere (secondary processes) or through gas-particle heterogeneous transformations. Through these processes various isomers of nitrated PAH analogues, such as nitropyrene and nitrofluoranthene, can be formed. The specific isomers that are formed are characteristic of certain types of formation processes and therefore are useful in determining the source origins of NPAHs.

Keywords Polycyclic aromatic hydrocarbon formation · Soot · Nitrated polycyclic aromatic hydrocarbons · Heterogeneous transformations · Particulate matter

2.1 Polycyclic Aromatic Hydrocarbon Formation: From Small Aliphatic Chains to Nascent Soot

Polycyclic aromatic hydrocarbons (PAHs) are molecules that contain two or more fused aromatic rings and are formed primarily through the incomplete combustion of organic materials (Ravindra et al. 2008). They are present in the environment through both natural and anthropogenic sources, though the latter constitutes the

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majority (Krauss et al. 2005). The mutagenic potential of PAHs is well known (Jung et al. 1991; Pashkin and Bakhitova 1979). Because PAHs are major constituents of soot, their formation from small aliphatic chains to soot aggregates is an active area of study.

PAH formation is dictated by a number of factors such as combustion temperature and pressure (Comandini et al. 2012; Yoon et al. 2008; Zhou et al. 2014) as well as fuel types, both aliphatic and aromatic fuels (Tregrossi et al. 1999; Hansen et al. 2016). While the experimental conditions may vary, in composite, a wide body of research has provided insight into the general mechanisms of soot formation. Broadly, this formation occurs through the initial decomposition of fuels, the subsequent production of initial aromatics from small aliphatic molecules, the nucleation to form larger PAHs and further growth and coagulation into larger soot particles (Richter and Howard 2000). For the purposes of this chapter, PAH formation is briefly discussed as a preface to discussion on the further transformation of PAHs into their nitrogenated analogues.

Pyrolytic processes above 500°C produce a number of reactive intermediates and radicals such as ethylene and acetylene which become the building blocks for constructing the initial aromatic rings (Llamas et al. 2017; Ravindra et al. 2008; Shukla and Koshi 2012). In general, the formation of the initial benzene ring is thought to occur through either the self-reaction between 3-carbon C_3H_3 species, the reaction between a 4-carbon species (n-C_4H_5, n-C_4H_3) and 2-carbon species or the reaction of a cyclopentadienyl (C_5H_5) with CH_3 (Frenklach 2002; Marinov et al. 1997, 1998; McEnally et al. 2006; Richter and Howard 2002; Shukla and Koshi 2012). While a number of precursor molecules can be involved, the type of fuel source decomposed will dictate which pathway is dominant (McEnally et al. 2006). For example, the reaction between two 3-carbon molecules in benzene formation is a dominant reaction in acetylene and ethylene flames (Richter and Howard 2002) and premixed propane (Marinov et al. 1997). Benzene, however, is not necessarily the first PAH formed. Naphthalene formation, through the self-reaction between C_5H_5 radicals, has been demonstrated and does not require the initial formation of benzene (Cavallotti and Polino 2013; Frenklach 2002; Marinov et al. 1997; Richter and Howard 2000).

After the formation of the initial ring(s), a number of mechanisms have been proposed for the further growth of PAHs, the most notable being the hydrogen abstraction-acetylene addition (HACA) pathway, which was generally thought to be the predominant route in PAH synthesis (Appel et al. 2000; Comandini et al. 2012; Frenklach 2002). HACA is a process where initial benzene rings and aliphatic hydrocarbon building blocks are converted to larger PAHs through an iterative process of hydrogen abstraction and acetylene (C_2H_2) additions (Frenklach 2002; Richter and Howard 2000). More specifically, the hydrogen abstraction of a hydrocarbon results in a radical that can react with C_2H_2 to form phenylacetylene which in turn forms the substrate for subsequent HACA steps to create the next ring (Comandini et al. 2012). Through this iterative process, PAHs can be built from benzene to naphthalene into larger PAH molecules (Frenklach 2002). Ultimately it is this procedure in the soot formation process that is the rate-controlling step in the further growth of soot (Frenklach 2002).

Though widely accepted as a mechanism for PAH growth, there is evidence that HACA is too slow and cannot be the sole factor involved (D'Anna and Violi 1998; Böhm et al. 1998; Richter and Howard 2002). Growth through methyl radical additions in a process similar to HACA has also been investigated (Hansen et al. 2016; Shukla et al. 2008; Yoon et al. 2008) as well as propargyl addition reactions (Raj et al. 2014; Slavinskaya and Frank 2009). An efficient method for the growth of PAHs is also seen through phenyl and benzene additions and can account for the rapid development of PAHs (Benish et al. 1996; Comandini et al. 2012; Constantinitis et al. 2015; Ono et al. 2015; Shukla et al. 2008) and is likely more efficient than HACA mechanisms. In aggregate, numerous studies are showing that there are a multitude of ways in which PAHs can grow from the initial aromatic ring(s) beyond HACA mechanisms and account for the rapid formation of soot particles.

From the creation of the first PAHs, reactions between PAHs and PAH radicals into larger PAHs (e.g. through dimerization and trimerization) form the basis for incipient soot which marks the transition into particulate matter (McKinnon and Howard 1992; Ono et al. 2015). The formation of initial soot particles is followed by their agglomeration to form larger soot particles and is followed by fractal spherical growth (Frenklach 2002). While much investigation has been performed on the formation of these initial rings, the transition from gas to particulate matter remains a poorly understood process (Frenklach 2002).

2.2 NPAHs and Their Formation from PAHs

While efforts to understand the mechanisms of PAH and soot formation are ongoing, there is also a concerted effort to understand the formation processes and environmental distributions of PAH derivatives such as the nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs). Research on NPAHs began when it was found that the mutagenicity of air pollution and diesel emissions could not be solely accounted for by PAHs (Pitts et al. 1978). This would ultimately lead to the discovery of the outsized contribution of NPAHs to air contaminant mutagenicity and has since been more closely investigated (Fu et al. 1985; Ishii et al. 2000; Pitts et al. 1978; Tokiwa et al. 1985), despite existing at levels between one and three orders less than their parent PAHs (Albinet et al. 2007; Bamford and Baker 2003; Wang et al. 2011). The increasing polarity of these NPAHs makes them more reactive with biological tissue and accounts for their disproportionate mutagenicity (De Guidi et al. 2012). For example, the dinitropyrenes (DNPs) possess a mutagenicity among the highest known (Arce and Morel 2013; Nakagawa et al. 1983) and therefore constitute a major toxicological threat. This outsized toxicity has created the imperative to include NPAHs in analyses that go beyond the EPA 16 PAHs that are routinely studied (Andersson and Achten 2015). Beyond toxicity however, their environmental fate differs from their parent PAHs, as they differ in parameters such as melting point, various partitioning coefficients (i.e. k_{ow}), vapour pressure and solubility.

The formation of NPAHs can be generalized as occurring through one of three routes: through direct emissions, through secondary atmospheric transformations and through gas-particle heterogeneous transformations. These different processes can produce distinct NPAH isomers that are characteristic of their sources, though as will be discussed, these distinctions are not always clear.

2.3 NPAH Formation Through Primary Combustion Processes

The primary production of NPAHs occurs through incomplete combustion processes and has been studied specifically within the context of diesel engine combustion (Bamford et al. 2003; Kameda et al. 2006; Karavalakis et al. 2012), though they can also form through gasoline engine combustion (Gibson 1983), coal combustion (Harris et al. 1984), biodiesel combustion (Llamas et al. 2017) as well as through cooking processes (Kinouchi et al. 1986). Primary transformation occurs as a result of the high temperatures and the electrophilic nucleation with NO_2^+ (Fu et al. 2012) as seen in the case of 1-nitropyrene (1-NP) formation from the PAH pyrene (Fig. 2.1).

Nitration occurs at the position of the molecule with the highest electron density to form 1-NP, and further nitration can produce the dinitropyrenes (DNPs) such as 1,3-DNP, 1,6-DNP and 1,8-DNP. As the NO_x species involved in the creation of these NPAHs is a function of temperature, the NPAH yield and composition are highly temperature dependent (Hayakawa 2016).

While a particular focus of NPAH studies has been on 1-NP (Bezebeh et al. 2003; Kojima et al. 2010), there is indication that 2-nitrofluorene (2-NF) may also appear in greater abundance (Beije and Möller 1988) as seen in heavy-duty diesel engines (Draper 1986). Beyond 1-NP and 2-NF, 3-nitrofluoranthene (3-NFr), 9-nitroanthracene (9-NA) and 6-nitrobenz[*a*]pyrene (6-NBaP) are also found in abundance in diesel exhaust and contribute to the exhaust mutagenicity (Bamford

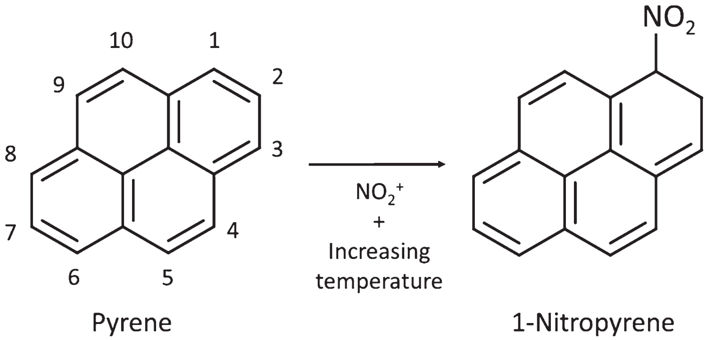

Fig. 2.1 The nitration of pyrene occurs at the site of the greatest electron density, producing a nitrated analogue at the first position

et al. 2003; Dimashki et al. 2000; Feilburg et al. 2001; Paputa-Peck et al. 1983; Salmeen et al. 1984; Schuetzle 1983). Furthermore, while certain NPAHs are used to characterize diesel emissions, the composition of diesel exhaust can change according to factors such as diesel particulate filters (Heeb et al. 2008) and biodiesel types (Karavalakis et al. 2010, 2011).

2.4 NPAH Formation Through Secondary Atmospheric Processes

While NPAHs formed through combustion processes comprise a significant component of atmospheric toxins, NPAHs can also be formed in the atmosphere, through gas-phase reactions. The atmospheric transformation of PAHs to NPAHs can occur via homogenous gas-phase reactions or secondary heterogeneous transformations of PAHs contained on particulate matter. The former is thought to constitute the majority of the atmospheric NPAHs (De Guidi et al. 2012; Reisen and Arey 2005) and involves nitration through reaction with NO_2 but is initiated by either OH or NO_3 radicals which form adducts that subsequently react with NO_2. The OH radicals are found in the troposphere (Vione et al. 2004) and form through reactions involving ozone:

$$O_3 + h\nu\left(\lambda < 320\right) \rightarrow O_2 + {}^{\bullet}O$$

$${}^{\bullet}O + H_2O \rightarrow 2\,{}^{\bullet}OH$$

Because this is a photochemical reaction and the ${}^{\bullet}OH$ radical rapidly degrades, this reaction occurs during the day (Arey 1998). One reported value for their abundance was modelled at 11.1×10^5 molecules/cm^3 (Naik et al. 2013). By contrast, the ${}^{\bullet}NO_3$ radical is formed primarily through a tropospheric reaction between O_3 and NO_2 (Geyer et al. 2001):

$$NO_2 + O_3 \rightarrow {}^{\bullet}NO_3 + O_2$$

The ${}^{\bullet}NO_3$ radical is prevalent during the night, as it otherwise undergoes rapid photolysis during the day and has undergone a significant increase since pre-industrial times (Khan et al. 2015). Ambient levels of the NO_3 radical have been difficult to quantify but, for example, have been observed to have a production rate between 4×10^5 cm^{3}s^{-1} and 8×10^6 cm^{3}s^{-1} at a site near Berlin, Germany (Geyer et al. 2001).

Whether via ${}^{\bullet}OH$ or ${}^{\bullet}NO_3$, both radicals attack the position of the molecule at the carbon position with the highest electron density (Zielinska and Samy 2006) to create an intermediate adduct that reacts with NO_2 to form a nitrated group at the *ortho* position, relative to the carbon initially attacked by the radical (Zielinska and Samy 2006; Atkinson and Arey 1994). This is followed by the removal of water or nitric

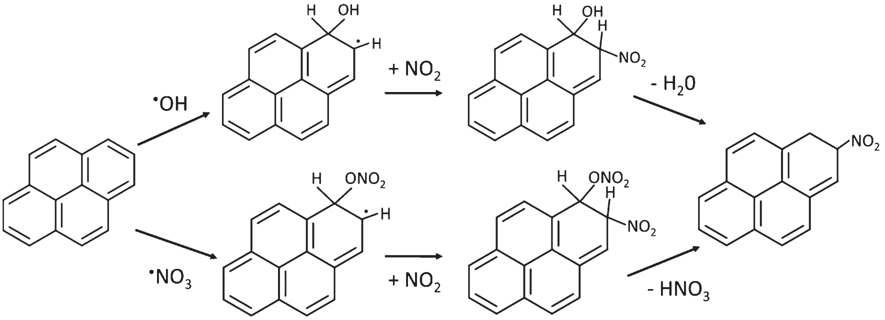

Fig. 2.2 The formation of 2-nitropyrene can occur through two mechanisms that differ in the radical that initially attacks the site of the greatest electron density. NO_2 will be added to the position *ortho* to this site

acid, depending on whether the initial radical is $^•OH$ or $^•NO_3$, respectively (Sasaki et al. 1997). The general formation in the case of pyrene transformation is summarized in Fig. 2.2.

Through these radical-assisted processes, the isomers of pyrene and fluoranthene (2-NP and 2-NFr) are the most commonly formed NPAHs and are not thought to form through combustion processes (Arey et al. 1986; Ciccioli et al. 1996; Kameda et al. 2006; Murahashi et al. 1999). However, the yields may differ from each other, with, for example, 2-NFr being produced in greater concentrations from $^•NO_3$ rather than $^•OH$ (Feilburg et al. 2001; Reisen and Arey 2005). While the formation of NP and NFr isomers in gas-phase reactions is studied extensively, other NPAHs such as nitrotriphenylenes (Kameda et al. 2006) and nitrobenzanthrones (Phousongphouang and Arey 2003) have also been examined and provide insight into the formation of otherwise lesser studied NPAHs.

2.5 NPAH Isomer Ratios as Source Indicators

Because of their differing formation mechanisms, NPAH isomers found in a sample are used as markers to identify the NPAH source. As mentioned above, 2-NP and 2-NFr are thought to form through the atmospheric transformations of parental PAHs and not through diesel combustion. By contrast 1-NP and 3-NFr are not thought to be formed through atmospheric reactions and are primarily combustion products, most notably found in diesel emissions (Kameda et al. 2006; Paputa-Peck et al. 1983). By using ratios of these specific isomers, it is possible to create values that can be used across different studies to identify the sources of NPAHs. For example, 2-NFr/1-NP ratios are commonly used in identifying whether atmospheric transformations or combustion products are the predominant source of NPAHs (Albinet et al. 2007; Bamford and Baker 2003; Lin et al. 2015; Marino et al. 2000; Wang et al. 2011). These ratios can be influenced by seasonality. For example, a study the Beijing atmosphere found that the lower 2-NFr/1-NP ratios in the winter could be attributed to increased coal and biomass combustion for heating purposes (Lin et al. 2015). The increased combustion that occurs in winter months and the influence this has on the distribution of NPAHs has been reported by many (Bandowe et al. 2014; Barrado et al. 2012; Sarti et al. 2017; Wada et al. 2001).

Furthermore, since $^{\bullet}NO_3$ radicals react with pyrene to form 2-NFr and negligible amounts of 2-NP, and $^{\bullet}OH$ radicals will form both 2-NFr and NP (Wei et al. 2012), 2-NFr/2-NP ratios are commonly used to approximate whether daytime OH or night-time NO_3 radical initiation is the more dominant driver of atmospheric NPAH creation (Albinet et al. 2007; Bamford and Baker 2003; Huang et al. 2014; Kameda et al. 2006; Marino et al. 2000; Reisen and Arey 2005; Wang et al. 2011). Values greater than 5 suggest a greater atmospheric secondary transformation, while values less than 5 suggest that primary emissions are dominant (Ciccioli et al. 1996; Wang et al. 2011). One study examined 2-NFr/2-NP concentrations at locations in Antarctica, Asia, Europe and South America and confirmed that these NPAHs were globally ubiquitous and formed from gases in the troposphere (Ciccioli et al. 1996). The utility of ratios like the 2-NFR/1-NP and 2-NFr/2-NP highlights the importance of being able to distinguish NPAH isomers, despite the inherent analytical challenges this may pose.

2.6 NPAH Partitioning onto Particulate Matter

Atmospheric PACs are associated primarily with particulate matter (PM), and numerous studies have found that the majority of PACs are found on finer and smaller $PM_{2.5}$ (Bozek et al. 2016; Di Filippo et al. 2010; Kong et al. 2010; Hayakawa et al. 1995; Kawanaka et al. 2008; Ohura et al. 2004; Tang et al. 2009). This is particularly alarming as $PM_{2.5}$ accounts for the majority of PM in the atmosphere (Lonati and Giugliano 2006) and is known to penetrate deeper into the respiratory system, creating not just a mechanical hazard but a greater toxicological threat (Bozek et al. 2016; Kawanaka et al. 2008). As a result of this toxicity, the PAH/NPAH associations with PM have been researched globally (Albinet et al. 2007; Barrado et al. 2012; Bozek et al. 2016; Dimashki et al. 2000; Marino et al. 2000; Wang et al. 2011; Wei et al. 2012).

In general, PACs have low vapour pressures, especially as molecular weight increases (Yaffe et al. 2001; Barrado et al. 2012). NPAHs in particular are more polar and have vapour pressures in general about 2–3 orders of magnitude less than PAHs, thus making condensation onto particulate matter more likely (Ciccioli et al. 1996; Heeb et al. 2008; Shen et al. 2012). An NPAH of a molecular weight equivalent to phenanthrene or less is more likely to exist in the gas phase, with 3–4 ring congeners such as NFr and NP (nominal mass: 247 g/mol) more likely to partition onto PM (Cochran et al. 2016; Yaffe et al. 2001). The structure of the sorption surface may also play a role. For example, in a study of PAH sorption to soot, it was found that the strong affinity for PAHs to soot is likely the result of π-π bonding as well as the planar structure of PAHs allowing them to penetrate deeper into the pores (Jonker and Koelmans 2002) and making them less available for reaction. Thus, being sorbed onto PM can protect the PAC from further gas-phase transformations, prolonging their atmospheric lifetimes and allowing for greater geographic dispersal. Sorption has also been shown to be dependant on weather, with colder weather causing greater partitioning onto aerosols such as PM, as a result of reduced vapour pressure and poor mixing of air (Bandowe et al. 2014; Ravindra et al. 2008). It should be noted, however, that the formation of PAH derivatives is driven by season, with winter having greater reactions with nitrogen oxides and summers having more photochemical reactions (Barrado et al. 2012). There is also the fact that winters have more fuel combustion occurring for heating purposes (Sarti et al. 2017). As a result, studies have shown that there is a greater concentration of PACs adsorbed onto PM in winter than in summer (Bandowe et al. 2014; Barrado et al. 2012; Ravindra et al. 2008; Sarti et al. 2017; Wada et al. 2001).

2.7 NPAHs and Particulate Matter: Heterogeneous Transformations

While it is believed that homogeneous gas-phase reactions, based on $^{\bullet}OH$ and $^{\bullet}NO_3$ radical intermediates, are the predominant routes for NPAH formation, there is a growing interest in understanding how PAHs sorbed onto atmospheric PM may be transformed by atmospheric oxidizing agents. This is especially salient, given the greater longevity and mobility of these PM-sorbed compounds.

The reactions of condensed PAHs with a number of gases such as O_3, OH, HNO_3 and $NO_3/N_2O_5/NO_3$ have been performed by many (Carrara et al. 2010; Gross and Bertram 2008; Jariyasopit et al. 2014; Kamens et al. 1990; Kwamena and Abbatt 2008; Perraudin et al. 2007; Wang et al. 2015; Zhang et al. 2011, 2014a, b; Zhou et al. 2015; Zielinska et al. 1986; Zimmermann et al. 2013) using a variety of sorption substrates such as quartz fibre filters (Cochran et al. 2016), natural aerosols (Ringuet et al. 2012) and mineral surfaces (Kameda et al. 2016), and the products of these heterogeneous reactions can differ markedly from gas-phase homogeneous reactions. The multitude of different gases and reaction substrates has produced a range of products. For this reason, the uptake of gases onto the particle surfaces has been performed to help understand the efficiency and likelihood of these transformations. Studies of this have been performed for gases such as O_3, OH, HNO_3, N_2O_5, NO_2 and NO_3 (Gross and Bertram 2008; Perraudin et al. 2007; Zhou et al. 2015).

For example, while it was initially thought that NO_3 had a minimal role in the heterogeneous transformations of PAHs and that N_2O_5 was the greater oxidizing agent (Pitts et al. 1985), more recently, there is evidence of a rapid uptake of NO_3 on soot surfaces (Mak et al. 2007). Furthermore, relative to NO_2 and O_3, NO_3 has been observed to have the highest reaction rate constants with particle-sorbed PAHs and that these reactions with NO_3 radicals are 4–5 orders faster than the gas-phase reactions (Liu et al. 2012). Similarly, the reaction of particle-associated PAHs with NO_3 was about four orders larger than with N_2O_5 or NO_2 despite existing in much lower concentrations (Gross and Bertram 2008).

In addition to the reacting gas, the actual substrate characteristics may also dictate the extent to which heterogeneous formation may occur. For example, Zhou et al. (2013) demonstrated that the secondary organic aerosols that comprise a significant part of $PM_{2.5}$ coatings can shield underlying contaminants such as PAHs from gas-phase oxidizing agents, thus shielding them from reaction over long transportation events. Another set of experiments showed that there was a difference in PAH reactivity with OH between graphite particles and combustion-derived surfaces, with the latter showing lower reactivity, possibly due to differences in site accessibility (Esteve et al. 2004, 2006).

Heterogeneous reactions can produce some of the NPAH isomers that characterize primary and secondary NPAH formation. For example, Zimmermann et al. (2013) found that reactions of ambient PM with $N_2O_5/NO_3/NO_2$ produced 1-NP, which they concluded was based on N_2O_5 reaction and not an NO_3 radical-assisted reaction. This would suggest an electrophilic nitration (Wang et al. 2015) and differs from the 2-NP isomer that would be expected from gas-phase reactions. Furthermore, 1-NP has also been formed through other heterogeneous processes, for example, through the reaction of NO_2 on mineral dust surfaces (Kameda et al. 2016) and silica particles (Miet et al. 2009) and OH reactions with aerosol particles (Ringuet et al. 2012). This contrasts with the belief that 1-NP is formed solely through combustion processes (viz. diesel engine combustion). Furthermore, Miet et al. (2009) also found that 1-NP sorbed onto silica particles could undergo transformation to form 1,3-DNP, 1,6-DNP and 1,8-DNP which correspond to the DNPs formed through electrophilic nitration. The formation of 2-NP and 2-NFr through heterogeneous interactions has been demonstrated as well (Ringuet et al. 2012; Zhang et al. 2014a, b; Zimmermann et al. 2013), showing that these isomers may not be specific to gas-phase transformations. For example, it was found that N_2O_5, with increasing humidity, could promote the formation of NO_2^+, which could produce the NP and NFr isomers characteristic of electrophilic nitration (Zhang et al., Zhang et al. 2014a, b). Studies of other NPAHs have also been performed, with, for example, studies on larger (five rings or greater) PAHs (Ishii et al. 2000; Jariyasopit et al. 2014). These studies of heterogeneous reactions suggest that the mechanisms of NPAH formation are more complicated than the primary/secondary source dichotomy presented earlier. However, although some of these reactions may call into question the use of marker isomers to identify primary and secondary NPAH formation, it should be noted that the heterogeneous transformations are likely to play a relatively minor role in PAH removal/transformation and so are unlikely to undermine the NPAH ratios discussed earlier.

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Part II
Analytical Methods

Chapter 3
PAHs/NPAHs

Ning Tang

Abstract The environmental atmosphere contains numerous kinds of organic pollutants. Among them are the polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs), which are carcinogenic and/or mutagenic. PAHs and NPAHs mainly originate from the imperfect combustion of organic matter such as coal, petroleum, and biomass. Both PAHs (having four rings or more) and NPAHs were detected in particulates from diesel- and gasoline-engine vehicles, and PAHs having lower molecular weights (three rings or less) were detected in the gaseous phase and unburned diesel fuel. PAHs and NPAHs were also detected in smoke from steel and iron industries, as well as in wastewater and sediment. In addition to the NPAHs such as 1,3-, 1,6-, 1,8-dinitropyrenes, and 1-nitropyrene (1-NP) that are emitted directly from the above sources, other important sources of NPAHs such as 2-NP and 2-nitrofluoranthene (2-NFR) are formed from the heterogeneous or homogeneous reactions of parent PAHs with nitrogen oxides and radicals in the atmosphere. PAHs and NPAHs need to be monitored because they are a health risk for humans and they are present throughout the environment. In this section, we review some reports on the analytical methods used in monitoring PAHs and NPAHs in the atmosphere.

Keywords PAHs · NPAHs · HPLC-FLD · HPLC-CLD · GC-MS/MS

3.1 Introduction

Several polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are carcinogenic and/or mutagenic (Ames et al. 1975; Epstein et al. 1979). The International Agency for Research on Cancer (IARC) has already ranked benzo[*a*]pyrene (BaP) and 1-nitropyrene (1-NP) as group 1

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(*carcinogenic to humans*) and 2A (*probably carcinogenic to humans*), respectively (IARC 2016). Furthermore, polycyclic aromatic ketones, such as 3-nitrobenzanthrone (3-NBA), have been shown to be strongly mutagenic and/or carcinogenic. The mutagenicity of 3-NBA is comparable to that of 1,8-dinitropyrene which is the strongest mutagen as tested by the *Ames* assay using *Salmonella typhimurium* TA98 and YG1024 strains. Several PAHs also exhibit estrogenic, antiestrogenic, and anti-androgenic activities (Kizu et al. 2000) or reactive oxygen species producing activity (Motoyama et al. 2009). Therefore, it is necessary to analyze PAHs and NPAHs, whose concentrations in the atmosphere are low but nevertheless show high toxicity. In this section, we review some reports about PAH/NPAH analytical methods.

3.2 Atmospheric Particulate Matter Sampling Methods

The partitioning of PAHs and NPAHs between gas and particulate phases in the atmosphere depends on several factors such as vapor pressure, temperature, atmospheric pressure, and the concentration and properties of dust (Keller and Terry 1984; Yamasaki et al. 1982). In the atmosphere, PAHs having two rings exist in the gas phase, PAHs having five rings or more exist in the particulate phase, and PAHs having three and four rings are in both phases (Araki et al. 2009). For the sampling of particulate-bound PAHs and NPAHs, air samplers equipped with quartz, glass, and Teflon filters have been commonly used (Goriaux et al. 2006; Hattori et al. 2007; Omar et al. 2002; Santos et al. 2016: Tang et al. 2011). One study has reported that there is significant formation of NPAHs during sampling periods and that this is due to the use of glass filters, rather than Teflon filters (Arey et al. 1988). However, other reports show that there is no evidence that different filters behave differently to produce this kind of artifact (Alfheim and Lindskog 1984; De Raat et al. 1990; Hart and Pankow 1990). Because the concentrations of NPAHs are very low in the atmosphere, a high-volume air sampler (300–1000 L/min) is used for collecting airborne particulates such as $PM_{2.5}$ (Albinet et al. 2007; Hayakawa 2000; Tang et al. 2005a). Several higher-level NPAHs (2-nitrofluorene, 9-nitroanthracene, 9-nitrophenanthrene, 3-nitrofluoranthene, 1-nitropyrene, 2,7-dinitrofluorene, 7-nitrobenz[*a*]anthracene, and 6-nitrochrysene) in the atmosphere can be collected by using a low-volume air sampler (38 L/min, 24 h) (Tutino et al. 2016). Because the concentrations of PAHs are usually higher than those of their corresponding NPAHs (Hayakawa 2016; Nassar et al. 2011; Tang et al. 2009), either low- or high-volume air samplers can be used. At high-level pollution sites such as industrial workplaces (Chaspoul et al. 2005) or kitchens (Chen et al. 2017), personal samplers (1–3 L/min) can be used to collect particulate-bound PAHs, NPAHs, and oxygenated derivatives. For example, the exposure of traffic police to PAHs during winter at intersections in Beijing, China, has been determined by using personal samples (Liu et al. 2007).

Atmospheric PAHs and NPAHs mainly originate from the imperfect combustion and pyrolysis of organic matter, although some NPAHs such as 2-nitropyrene and 2-nitrofluoranthene are formed via atmospheric reactions of their parent PAHs

(Arey et al. 1986; Hayakawa et al. 1995; Rogge et al. 1993). Because most particulate-bound PAHs and NPAHs existing in $PM_{2.5}$ have a relevant health risk, different size fraction devices have been developed for the selective collection of $PM_{2.5}$. High-volume air samplers with a single- or multistaged cascade have frequently been used for $PM_{2.5}$ (Alves et al. 2016; Lung and Liu 2015; Zhang et al. 2016). Previous reports have been carried out with medium-volume samplers (100 L/min) and personal sampler impactors (5 L/min) (Mohammed et al. 2016; Wang et al. 2016). The use of other multistaged cascades has also been reported (Kawanaka et al. 2004; Tang et al. 2009).

PAHs and NPAHs are not only subjected to photodegradation (Hayakawa et al. 2000) but are degraded by ozone, nitrate, and hydroxyl radicals in the atmosphere (Tsapakis and Stephanou 2007). In order to minimize this oxidation, denuder sampling devices have been developed (Delgado-Saborit et al. 2013; Lane and Gundel 1996; Liu et al. 2006; Temime-Roussel et al. 2004). These can remove oxidizing gasses from the air stream prior to the collection of particulates on the filter. The atmospheric PAH concentrations measured using conventional samplers not equipped with an ozone trap have been underestimated by more than 200% (Goriaux et al. 2006).

3.3 Pretreatment Methods of Collected Samples

For extracting PAHs and NPAHs from airborne particulates, solvent-based methods have been mainly used and are discussed in our previous review (Hayakawa 2000). Soxhlet (Larsen and Baker 2003; Sanderson and Farant 2000) and ultrasonic (Morisaki et al. 2016; Tang et al. 2016; Wang et al. 2016) extractions are the most popular for extracting soluble organic compounds including PAHs and NPAHs. These methods have been improved by several modifications of solvents and extraction times. An ultrasonic extraction system with 500 μL of an acetonitrile-dichloromethane mixture (18% of acetonitrile in dichloromethane) was used for extracting 18 PAHs, 27 NPAHs, and 5 OPAHs from airborne particulates (Santos et al. 2016). Recently, other solvent-based methods, such as an accelerated solvent extraction system (ASE) and microwave extraction system (MWE), have been developed in order to reduce the extraction time and solvent volumes. ASE extracted 26 parent and alkyl-PAHs, 4 azaarenes, and total 15 NPAHs and OPAHs from airborne particulates by using dichloromethane or a mixture of acetone-dichloromethane (2:1 v/v) (Alves et al. 2016). Toluene and methanol have also been used to extract PAHs and OPAHs (Ahmed et al. 2015). By using a mixture of acetone-hexane (1:1 v/v), MWE can extract 14 NPAHs (Tutino et al. 2016) and 12 NPAHs and 4 OPAHs (Chen et al. 2017). After liquid extraction, solid-phase extraction with silica gel and/or C_{18} cartridges is usually used for the cleanup of samples. Supercritical fluid extraction is another useful extraction technique. For example, PAHs and NPAHs were quantitatively extracted from airborne particulates by using dichloromethane as a modifier to CO_2 (Shimmo et al. 2004). NPAHs and OPAHs were selectively extracted using toluene as a modifier to CO_2 (Castells et al. 2003).

In recent years, gas chromatography (GC) has become a common analytical technique for simultaneous separation of PAHs, NPAHs, and OPAHs. Therefore, thermal extraction methods such as direct thermal desorption (Chow et al. 2007; Ho and JZ 2004) and Curie point pyrolysis extractions (Neususs et al. 2000) have also been developed.

3.4 Determination of PAH Concentrations

Approximately 33 kinds of PAHs have been determined in environmental samples (Ma et al. 2013; Feng et al. 2012). The US-EPA (US Environmental Protection Agency) 16 priority PAHs (2–6 rings) have been extensively studied (Fig. 3.1). Chromatographic techniques including GC and high-performance liquid chromatography (HPLC) have been commonly used for the determination of PAHs in the environment. For the analysis of PAHs in airborne particulates, GC-mass spectrometry (GC-MS) in the electron impact (EI, 70 eV) mode and HPLC-fluorescence detection (HPLC-FL) are the most common methods (Araki et al. 2009; Chen et al. 2011; Liu et al. 2007; Zhang et al. 2010). Applications of these methods include all or some of the EPA 16 priority PAHs (Ma et al. 2013; Tang et al. 2015; Xu et al. 2015; Zhang et al. 2016) and WHO (World Health Organization) 17 PAHs (Feng et al. 2012; Hong et al. 2016; Omar et al. 2002) as their carcinogenicity and/or

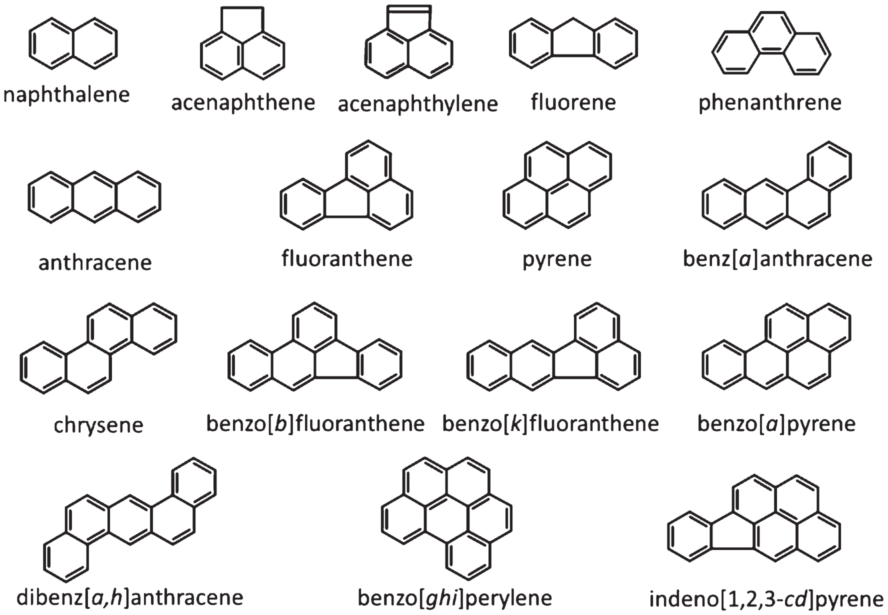

Fig. 3.1 Structures of the 16 US-EPA priority PAHs

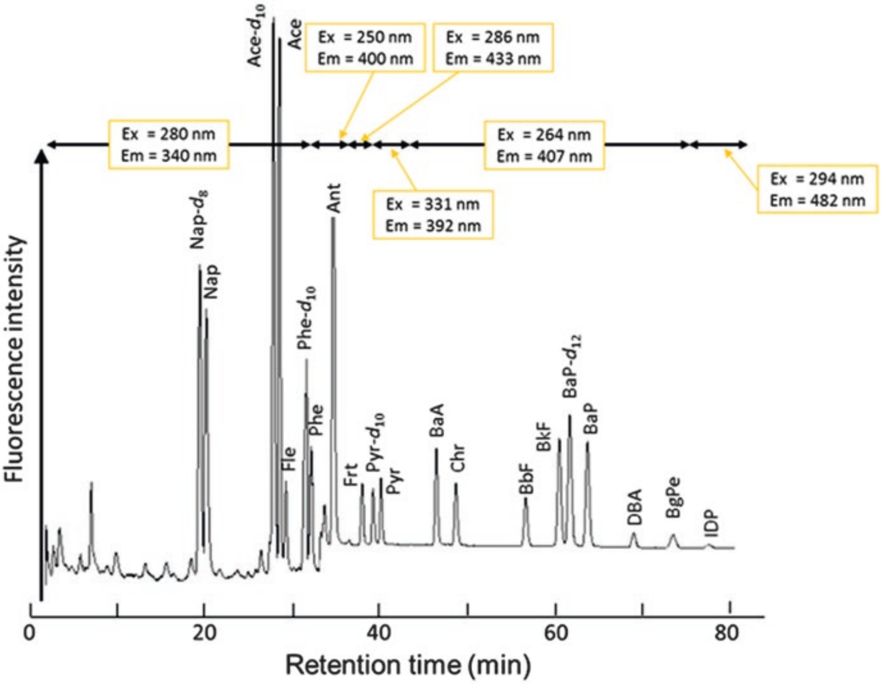

Fig. 3.2 A chromatogram of 15 of the US-EPA 16 priority PAHs extracted from an environmental sample and analyzed using HPLC-FL
NaP, Naphthalene; Ace, acenaphthene; Fle, fluorene; Phe, phenanthrene; Ant, anthracene; Frt, fluoranthene; Pyr, pyrene; BaA, benz[*a*]anthracene; Chr, chrysene; BbF, benzo[*b*]fluoranthene; BkF, benzo[*k*]fluoranthene; BaP, benzo[*a*]pyrene; DBA, dibenz[*ah]*anthracene; BgPe, benzo[*ghi*]perylene; IDP, indeno[1,2,3-*cd*]pyrene
NaP-d_8, Phe-d_{10}, Pyr-d_{12}, and BaP-d_{12}, labeled PAHs as internal standards

mutagenicity are well known. Figure 3.2 shows a chromatogram of PAHs extracted from environmental samples by using HPLC-FL. Fifteen kinds of US-EPA priority 16 PAHs were easily and sensitively determined, except for acenaphthylene because it is a non-fluorescent substance. Recently, GC-MS and HPLC-FL methods have been used for determining benzo[*c*]fluorene, whose relative potency factor with respect to the mutagenicity of BaP is about 20 times as toxic as reported by the US-EPA (Yagishita et al. 2015; Morisaki et al. 2016). On the other hand, other minor methods include GC-electron capture detection, LC-GC-MS (Christensen et al. 2005), HPLC-ultraviolet (HPLC-UV) (Cheng et al. 2007), HPLC-photodiode array (Liu et al. 2009), and HPLC-FL/UV (Albinet et al. 2007) detection methods are also used to identify PAHs in the atmosphere.

3.5 Determination of NPAHs

Figure 3.3 shows the structures of typical NPAHs in the atmosphere. Concentrations of these NPAHs are much lower than those of their parent PAHs. The analytical methods available for NPAH detection in airborne particulates are limited to several chromatographic methods such as GC and HPLC as described in our previous report (Hayakawa 2000). Among them, GC-MS with negative ion chemical ionization (GC/NICI-MS) (Alves et al. 2016; Kawanaka et al. 2004; Ringuet et al. 2012), GC-MS (Tutino et al. 2016), and HPLC-chemiluminescence detection (HPLC-CLD) (Hayakawa et al. 1991, 2001, 2011a; Tang et al. 2003, 2004, 2005b, 2014) are mostly used (Fig. 3.4). By using HPLC-CLD, we have identified the environmental levels, compositions, and main sources of NPAHs in cities located in the East Asian area (Hayakawa 2016; Tang et al. 2005a).

Because atmospheric samples contain not only NPAHs but also oxygenated PAHs (OPAHs) and have been recognized as similarly or more toxic than their parent PAHs (Bekki et al. 2012; Hayakawa et al. 2007, 2011b; Motoyama et al. 2009), several sensitive analytical methods for determining OPAHs and/or the simultaneous determination of PAHs, NPAHs, and OPAHs have been developed in recent years. Thirty-seven OPAHs in the airborne particulates were identified by gas chromatography-tandem mass spectrometry, following a one-pot reductive trimethylsilyl derivatization (Toriba et al. 2016). GC/NICI-MS (Alves et al. 2016; Chen et al. 2017; Huang et al. 2014; Ringuet et al. 2012) has been applied to simultaneously determine PAHs,

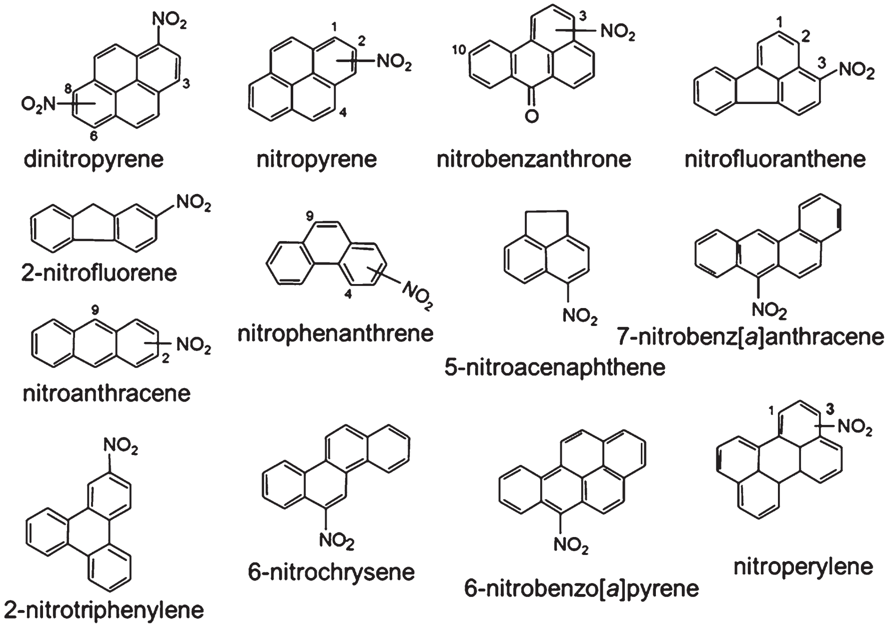

Fig. 3.3 Structures of typical NPAHs in the atmosphere

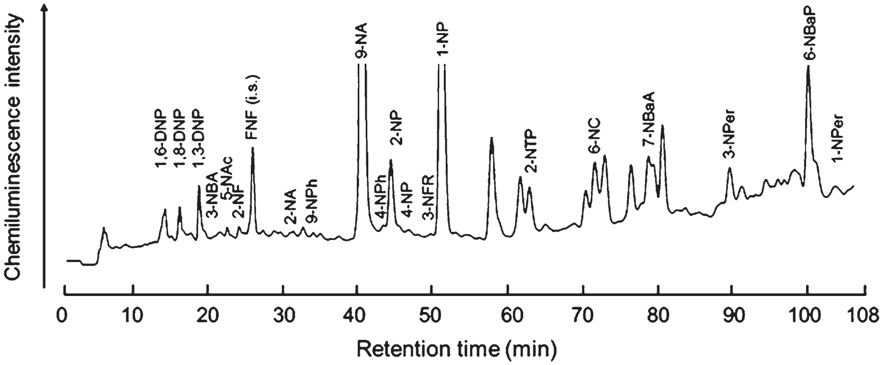

Fig. 3.4 A chromatogram of 21 kinds of NPAHs extracted from environmental samples and detected using HPLC-CL
1,3-, 1,6-, and 1,8-DNP, dinitropyrene; 3-NBA, 3-nitrobenzanthrone; 5-NAc, 5-nitroacenaphthene; 2-, 9-NF, nitrofluorene; 4-, 9-NPh, nitrophenanthrene; 1-, 2-, 4-NP, nitropyrene; 3-NFR, 3-nitrofluoranthene; 2-NTP, 2-nitrotriphenylene; 6-NC, 6-nitrochrysene; 7-NBaA, 7-nitrobenz[*a*]anthracene; 6-NBaP, 6-nitrobenz[*a*]pyrene; 1-, 3-NPer, nitroperylene; FNF, 2-fluoro-7-nitrofluorene as an internal standard

NPAHs, and OPAHs in the atmospheric particulates. Furthermore, methods based on LC-MS/MS for PAHs and NPAHs (Lung and Liu 2015), LC-GC-MS for NPAHs and OPAHs (Ahmed et al. 2015), and GC-multiphoton ionization/TOF-MS (Imasaka 2013; Tang et al. 2016) may be more promising because of their high selectively and sensitivity.

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Chapter 4

Analytical Methods for Oxidative Derivatives of PAHs Including Application to Environmental and Biological Samples

Akira Toriba

Abstract Oxidative derivatives of PAHs such as hydroxylated PAHs (OHPAHs) and PAH quinones (PAHQs) and other oxidized derivatives have been observed in environmental samples such as airborne particulate matter (PM), soil, sediment, seawater, and wastewater. They have been mainly analyzed by gas chromatography with mass spectrometry (GC-MS) with electron impact (EI) ionization after trimethylsilyl (TMS) derivatization. A reductive TMS derivatization for determining PAHQs achieved a considerable improvement in their detection sensitivity with EI mode. Biomarkers have been used for the evaluation of personal exposure to PAHs through the measurements of PAH metabolites in biological samples such as urine. PAHs incorporated into the human body are converted to phenols, and their glucuronide and/or sulfate conjugates are excreted in urine. Urinary 1-hydroxypyrene and 3-hydroxybenzo[*a*]pyrene have been frequently analyzed by HPLC with fluorescence detection and LC-MS/MS. The urinary metabolites of oxidative derivatives of PAHs (9,10-phenanthrenequinone) and nitro-derivatives of PAHs (1-nitropyrene) were identified by LC-MS/MS and suggested as a new type of biomarker for PAH exposure.

Keywords Polycyclic Aromatic Hydrocarbons (PAHs) · Oxidized PAH derivatives · Reactive oxygen species · Metabolite · Urinary biomarker

4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their nitro-derivatives (NPAHs) are well known to be carcinogenic/mutagenic to humans (Lewtas 2007). Recent studies have drawn attention to the endocrine disruption potential (Hayakawa et al. 2007, 2011) and the reactive oxygen species (ROS) production, caused by oxidative derivatives of PAHs (Bolton et al. 2000). A comprehensive analysis of PAH derivatives

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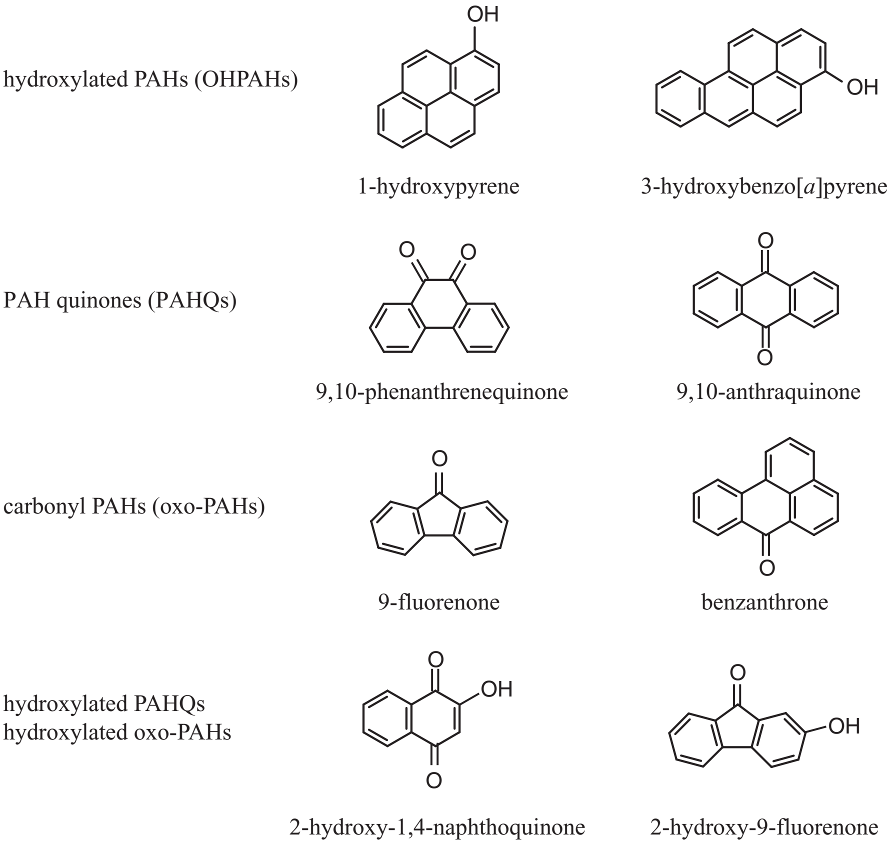

Fig. 4.1 Structures of representative oxidative derivatives of PAHs

using mass spectrometric techniques has become mainstream because some derivatives may induce similar or strong adverse health effects compared to parent PAHs (Lewtas 2007). Oxidative derivatives of PAHs such as hydroxylated PAHs (OHPAHs) and PAH quinones (PAHQs) and other oxidized derivatives such as carbonyl PAHs (oxo-PAHs), hydroxylated PAHQs, and hydroxylated oxo-PAHs have been observed in environmental samples such as airborne particulate matter (PM), soil, sediment, seawater, and wastewater. The structures of representative oxidative PAH derivatives are shown in Fig. 4.1. Furthermore, various metabolites of PAHs such as OHPAHs and PAHQs are generated through animal metabolic processes and have been determined in biological fluids such as urine. In particular, urinary 1-hydroxypyrene has been widely used as a biomarker to evaluate exposure to PAHs in epidemiological studies (Hansen et al. 2008).

4.2 Analytical Methods for OHPAHs in Environmental Samples

OHPAHs in atmospheric and combustion source samples have been analyzed mainly by gas chromatography with mass spectrometry (GC-MS) with electron impact (EI) ionization after trimethylsilyl (TMS) derivatization (Wang et al. 2007a, b; Cochran et al. 2012; Bandowe et al. 2014a, b) or GC-MS with negative chemical ionization (NCI) mode after pentafluorobenzoyl derivatization (Ma et al. 2016; Lin et al. 2015). Through method development using liquid chromatography with mass spectrometry (LC-MS) or LC (UPLC) with tandem mass spectrometry (LC-MS/MS), researchers discussed appropriate ionization methods. The atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) modes gave high ionization efficiency for OHPAHs, whereas the electrospray ionization (ESI) mode is applicable to their detection (Grosse and Letzel 2007). Several OHPAHs in woodsmoke particulate samples were quantified by LC or UPLC-MS/MS methods (Avagyan et al. 2015, 2016). In addition to mass spectrometry detection, HPLC-based techniques with electrochemical detection (ECD) (Galceran and Moyano 1995), fluorescence detection (FL) (Barrado et al. 2012), and chemiluminescence detection (Li et al. 2011) have also been applied to several compounds in atmospheric particulates.

Several studies reported the existence of OHPAHs in ambient PM samples and combustion sources; however, the target compounds were markedly limited compared with parent PAHs. OHPAHs can be emitted from incomplete combustion such as biomass burning and vehicle exhaust (Avagyan et al. 2016; Cochran et al. 2012; Ma et al. 2016; Lin et al. 2015) and generated as a result of atmospheric photochemical reactions of the parent PAHs (Pozzoli et al. 2004; Keyte et al. 2013). However, the details of their secondary formation in the atmosphere are still unclear.

In addition to atmospheric particulate matter, OHPAHs have been identified in seawater, sewage, soil, and sediment samples. A GC-MS method with TMS derivatization was applied to analyze OHPAHs in seawater samples, and the total concentrations of detected OHPAHs were in the range between 38.7 and 1074 ng L^{-1} (Wang et al. 2016a, b). Several kinds of OHPAHs in the dissolved phase and in suspended solids of wastewater treated in a sewage treatment plant were analyzed by GC-ESI-MS, and their total concentrations ranged from 15 to 68 ng L^{-1} (Pojana and Marcomini 2007). 2-hydroxynaphthalene, 1-hydroxyacenaphthene, and 9-hydroxyfluorene in urban soils were determined by GC-MS with TMS derivatization, and their concentrations were much lower than the parent PAHs in the soil samples (Bandowe et al. 2011). In Hong Kong mangrove sediments, 2-hydroxyfluorene was a dominant OHPAH among eight analytes determined by GC-MS with silylation by *N*-(tert-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) (Wang et al. 2012, 2015). The detected OHPAHs probably originated from biodegradation and accumulated in the sediment.

4.3 Analytical Methods for PAHQs in Environmental Samples

PAHQs have been reported to overproduce ROS through a redox cycle (Bolton et al. 2000; Taguchi et al. 2007). Unstable semiquinone radicals are produced by enzymatic reduction reactions of PAHQs and subsequently generate $O_2^{\bullet -}$ under the presence of molecular oxygen when being reoxidized to quinone. In the redox cycling process, PAHQs function as a catalyst, causing the overproduction of ROS. ROS production has the potential to induce oxidative stress. Therefore, exposure to PAHQs in the environment is suspected to have adverse effects on human health.

To monitor atmospheric concentrations of PAHQs, analytical methods based on LC-MS or LC-MS/MS have typically been accomplished through PAHQ ionization in the APCI mode (Jakober et al. 2006; Mirivel et al. 2010; O'Connell et al. 2013; Lintelmann et al. 2006; Delhomme et al. 2008; Walgraeve et al. 2012). In HPLC methods using optical detections, PAHQs were converted to fluorescence derivatives (Kishikawa et al. 2004), and the ROS production ability of PAHQs was applied to their chemiluminescence detection (Ahmed et al. 2009). However, HPLC methods have only been applied to limited kinds of PAHQs. GC-MS methods were preferred in the analysis of environmental samples (Cho et al. 2004; Delgado-Saborit et al. 2013; O'Connell et al. 2013; Layshock et al. 2010; Sousa et al. 2015; Nocun and Schulze 2013; Ahmed et al. 2015), even though most GC-MS methods need acetyl derivatization to improve sensitivity. More recently, a GC-MS/MS method for determining 37 PAHQs in atmospheric samples has been developed, and the adopted reductive TMS derivatization achieved a considerable improvement in their detection sensitivity (Toriba et al. 2016). A representative chromatogram of the TMS-derivatized PAHQs is shown in Fig. 4.2. On the other hand, GC-NCI-MS provided a practical direct detection of PAHQs without derivatization (Albinet et al. 2006, 2014; Keyte et al. 2016).

Like PAHs, PAHQs are generated through incomplete combustion and subsequently released to the atmosphere and have been reported as a typical organic substance included in airborne PM and gas phases (Andreou and Rapsomanikis 2009; Bandowe et al. 2014a, b; Delgado-Saborit et al. 2013; Eiguren-Fernandez et al. 2008a; Wei et al. 2015; Wingfors et al. 2011). Diesel particulate matter is considered as a primary source of PAHQs (Cho et al. 2004; Jakober et al. 2007), whereas secondary formation from reactions of PAHs with ozone and radical species in the atmosphere has been reported (Wang et al. 2007a, b; Eiguren-Fernandez et al. 2008b; Lee et al. 2015). However, the mechanisms behind primary and secondary formation are not clearly understood.

In addition to atmospheric samples, PAHQs in urban soil samples (Bandowe et al. 2010, 2011 and 2014a, b) and soils from remote forests (Obrist et al. 2015) were determined using GC-MS. Soil samples were extracted by pressurized liquid extraction, followed by a cleanup of extracts using silica gel chromatography. 9,10-Anthraquinone (9,10-AQ) was a predominant PAHQ in the soils (Bandowe et al. 2011, 2014a, b; Obrist et al. 2015). The concentration ratios of some PAHQs

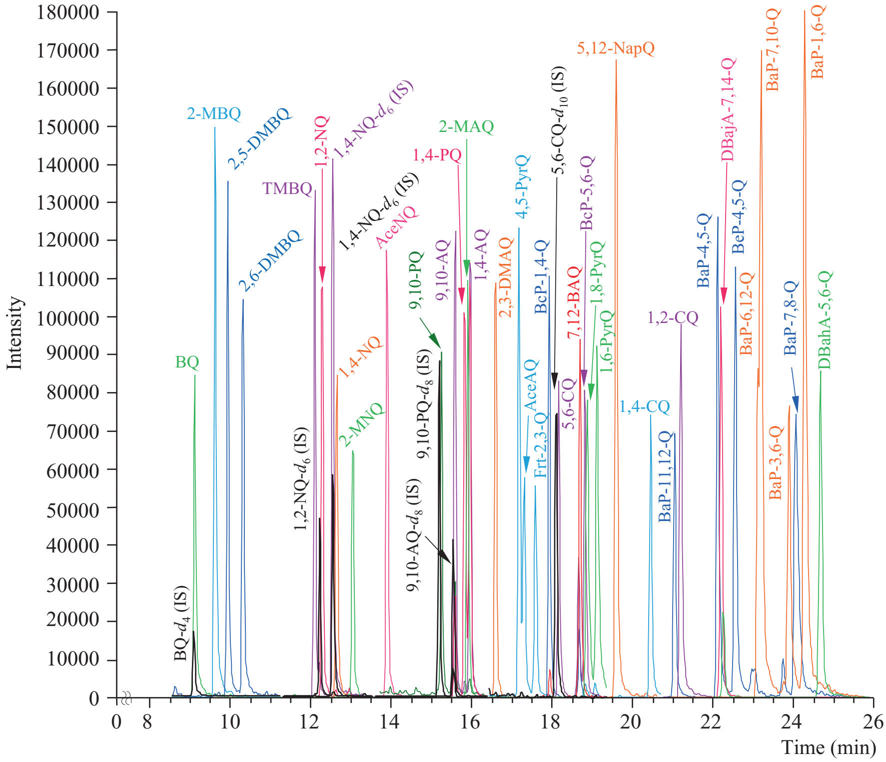

Fig. 4.2 Representative SRM chromatograms of TMS-derivatized PAHQ standards by a GC-MS/MS method (Toriba et al. 2016)

to their parent PAHs in the soils were higher than 1 as a result of photochemical and microbial degradation of parent PAHs (Bandowe et al. 2011, 2014a, b). Han et al. (2015) and Wang et al. (2015) measured PAHQs in sediment samples using GC-MS after pressurized liquid extraction and further purification and derivatization steps, and both reports showed high concentrations of 1,2-acenaphthenequinone and 9,10-AQ.

4.4 Analytical Methods for Other Oxidized Derivatives in Environmental Samples

Oxo-PAHs such as 9-fluorenone (9-Flo), benzanthrone, and 6H–benzo[*c,d*]pyrene-6-one (6H–BcdPO) are other major monitored components and have been determined by GC-NCI-MS (Albinet et al. 2006, 2014; Wang et al. 2016a, b). 9-Flo and 6H–BcdPO were the most abundant oxidized derivatives in emissions of oxo-PAHs from coal combustion (Wang et al. 2016a, b). Hydroxylated PAHQs

(2-hydroxy-1,4-naphthoquinone, 1,8-dihydroxyanthraquinone) and hydroxylated oxo-PAHs (2-hydroxy-9-fluorenone) were also detected in woodsmoke PM, but not in diesel exhaust (Cochran et al. 2012; Cochran and Kubátová 2015) and ambient PM samples (Wang et al. 2007a, b). Their hydroxy group(s) were converted into their TMS ethers and then analyzed by GC-MS.

Oxo-PAHs in soil samples were analyzed by GC-ESI-MS, and the composition of oxo-PAHs in urban soils was dominated by 9-Flo and 1-indanone (Bandowe et al. 2010, 2011 and 2014a, b). They reported increased ratios of the two compounds to their parent PAHs and hypothesized that their enhanced formation was due to the tropical environment of Bangkok, with higher solar irradiation and temperature (Bandowe et al. 2014a, b). Similarly, the high ratio of 9-Flo to fluorene was observed in soils from remote forests (Obrist et al. 2015). Five oxo-PAHs in mangrove sediments were analyzed by GC-MS and 9-Flo, in addition to 9,10-AQ, and showed higher concentrations than their parent PAHs in some samples (Wang et al. 2015).

4.5 Metabolites of PAHs, PAHQs, and NPAHs

Sampling of PAHs and their various derivatives at a fixed outdoor location has limitations in evaluating personal exposure. Therefore, PAH concentrations inhaled by individuals have been monitored by using personal air samplers. However, there are inherent difficulties in examining human individuals. There are a wide variety of PAH sources, and differences exist in personal lifestyles (such as smoking and dietary habits) and a number of human body functions such as absorption, distribution, and excretion that make studies of humans difficult. Furthermore, wearing a mini pump and an impactor for personal monitoring is often troublesome. Because of this, biomarkers have been developed to evaluate PAH exposure level through the measurements of PAH metabolites in biological samples such as urine.

PAHs incorporated into the human body are converted to phenols and dihydrodiols by cytochrome P450-dependent monooxygenases. In addition, one part of the dihydrodiols is converted into dihydrodiol epoxides by additional oxidation. In the case of benzo[*a*]pyrene, benzo[*a*]pyrene-7,8-diol-9,10-epoxide produced through metabolism binds to guanine and adenine bases in DNA and induces DNA mutations. On the other hand, phenols and dihydrodiols are excreted in urine or bile in the form of glucuronide and sulfate conjugates (Jongeneelen 1997). The phase II conjugating enzymes, uridine 5′-diphosphate (UDP)-glucuronosyltransferases (UGTs), catalyze the *O*-glucuronidation of phenols and dihydrodiols, and the glucuronidation represents an important pathway in the elimination of PAHs (Wells et al. 2004). PAH metabolites have been determined as biomarkers to evaluate human exposure to PAHs. Among them, urinary 1-hydroxypyrene (1-OHPyr) has been frequently used as a biomarker for PAH exposure. Pyrene is metabolized into the intermediary 1-OHPyr to form 1-hydroxypyrene-glucuronide and/or sulfate, which are excreted in urine.

An HPLC-FL method for determining 1-OHPyr established in 1987 became the most commonly used method (Jongeneelen et al. 1987). This requires an enzymatic hydrolysis step to deconjugate the glucuronide and sulfate of 1-OHPyr. For quantitative determination, a standard addition method has generally been used; however, more than two measurements for each sample are needed, and the analysis takes significant time to complete. To avoid this inconvenience, an HPLC method that uses deuterated 1-OHPyr as an internal standard has been developed (Chetiyanukornkul et al. 2002). Recently, many analytical procedures using HPLC with fluorescence detection (Toriba et al. 2003; Chetiyanukornkul et al. 2006; Barbeau et al. 2011), GC-(HR)MS(/MS) with silylation (Woudneh et al. 2016; Li et al. 2014), or LC(UPLC)-MS(/MS) with (Jacob et al. 2007; Luo et al. 2015) or without derivatization (Onyemauwa et al. 2009; Lankova et al. 2016) have been developed to determine urinary 1-OHPyr and other PAH metabolites having 4–5 rings, which are important for PAH exposure assessments. In particular, the detection of urinary 3-hydroxybenzo[*a*]pyrene (3-OHBaP), a major metabolite of benzo[*a*]pyrene (BaP), has been of particular interest as a biomarker for PAH exposure because a metabolite of carcinogenic PAHs is preferable to 1-OHPyr from noncarcinogenic pyrene. However, environmental exposure to BaP is lower than pyrene, and there are various metabolic and excretion pathways; therefore, the levels of urinary 3-OHBaP were within ng/L concentrations. Urinary 3-OHBaP in human urine samples has been successfully determined by HPLC with fluorescence detection (Barbeau et al. 2011) and LC-MS/MS with derivatization (Luo et al. 2015; Yao et al. 2014; Sarkar et al. 2009).

The abovementioned GC-MS and some LC-MS/MS methods require a derivatization step in addition to the hydrolysis (deconjugation) step; therefore, direct measurements of 1-hydroxypyrene-glucuronide (1-OHPyr-G) have also been undertaken to simplify the pretreatment of urine samples. 1-OHPyr-G levels in human urine account for more than 80% of total pyrene metabolites (Singh et al. 1995) and are sufficient to evaluate PAH exposure. An HPLC-FL method detected 1-OHPyr-G by taking advantage of its 3–5 times higher fluorescence than unconjugated 1-OHPyr (Singh et al. 1995). An LC-MS/MS using a specific fragmentation of the glucuronide sugar moiety on ESI mode has been developed for determining 1-OHPyr-G (Kakimoto et al. 2008). The methods do not require time-consuming hydrolysis and derivatization steps.

There are a few studies on the measurement of PAHQ metabolite(s) in biological samples. 9,10-Phenanthrenequinone (9,10-PQ), one of the PAHQs with the ability to produce ROS, is metabolized to 9,10-dihydroxyphenanthrene (9,10-PQH$_2$) by NAD(P)H quinone oxidoreductase (NQO1) and aldo-keto reductase (AKR) through two-electron reduction pathways (Fig. 4.3). In vitro, once 9,10-PQH$_2$ is formed by the reduction, its conjugation by UGTs could terminate redox cycling of the quinone, and the monoglucuronide of 9,10-PQH$_2$ (9,10-PQHG) is transported into extracellular space (Taguchi et al. 2008). In recent years, 9,10-PQHG have been identified as a metabolite of 9,10-PQ in human urine, directly confirming PAHQ exposure through respiration (Asahi et al. 2014). The exposure level of phenanthrene (Phe) should be much higher than that of 9,10-PQ due to their atmospheric levels (Eiguren-Fernandez et al. 2008b). The metabolic pathway from Phe to 9,10-Phe-dihydrodiol (Phe-diol) is a minor route (Grimmer et al. 1997), and

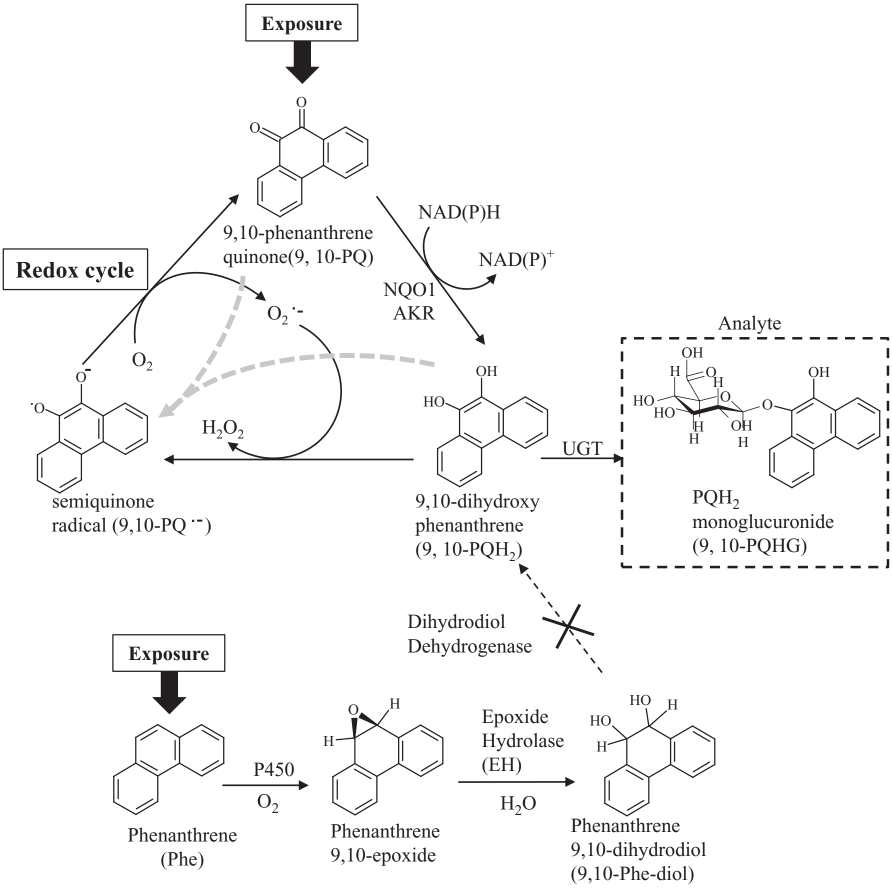

Fig. 4.3 Metabolic pathways of 9,10-PQ and phenanthrene to 9,10-PQHG
NAD(P)H quinone oxidoreductase, NQO1; aldo-keto reductase, AKR; UGT, UDP-glucuronyltransferase

dihydrodiol dehydrogenases, members of AKR superfamily, regioselectively oxidize non-K region trans-dihydrodiols but are inactive on K region trans-dihydrodiols such as 9,10-Phe-diol (Bolton et al. 2000; Palackal et al. 2001; Zhang et al. 2012). Urinary 9,10-PQHG originates from only direct exposure to atmospheric 9,10-PQ without consideration of exposure to 9,10-PQ through the metabolic pathway of Phe (Fig. 4.3). Urinary 9,10-PQHG should be useful to evaluate 9,10-PQ (PAHQs) exposure and the health effects of ROS upon exposure.

Among NPAHs, 1-nitropyrene (1-NP) is one of the most abundant NPAHs in diesel exhaust particulates (DEP); therefore, the metabolites of 1-NP are a specific biomarker of DEP exposure (Zielinska et al. 2004). The metabolic pathway of 1-NP has been studied using various tissues and species and consists of two major routes: cytochrome P450-mediated C oxidation and the reduction of the nitro group

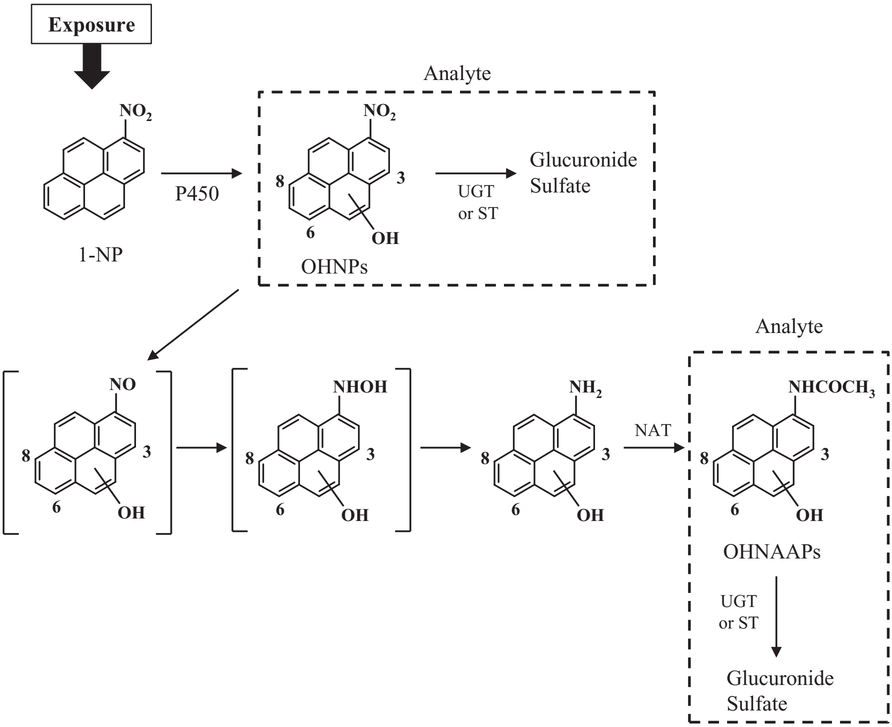

Fig. 4.4 Major metabolites of 1-NP in human urine
P450, cytochrome P450; NAT, N-acetyltransferase; UGT, UDP-glucuronyltransferase; ST, sulfotransferase

(Fig. 4.4). Some intermediates have been shown to covalently bind to DNA or proteins. Animal studies identified hydroxy-1-nitropyrenes (OHNPs), hydroxy-*N*-acetyl-1-aminopyrenes (OHNAAPs), *trans*-4,5-dihydro-4,5-dihydroxy-1-nitropyrene, *N*-acetyl-1-aminopyrene, and 1-aminopyrene as urinary or fecal metabolites (Ball et al. 1984; El-Bayoumy et al. 1984; Howard et al. 1995).

In humans, only a few studies have reported methods for determining urinary 1-aminopyrene as a metabolite of 1-NP (Grimmer et al. 2000; Seidel et al. 2002; Laumbach et al. 2009). Although 1-NP metabolites such as OHNPs and OHNAAPs were expected to be the major metabolites from previous studies (Fig. 4.4), they have never been detected in human urine, due to their low concentrations in human urine and the insufficient sensitivity of conventional analytical methods. An LC-MS/MS method was developed for the simultaneous measurement of the urinary 1-NP metabolites, intended to be biomarkers of low-level 1-NP (DEP) exposure in humans (Toriba et al. 2007). This report was the first to demonstrate the presence of OHNAAPs and OHNPs in human urine. Almost all the 1-NP metabolites in human urine are present as glucuronide and/or sulfate conjugates. The conjugates were hydrolyzed enzymatically, followed by LC-MS/MS analysis. Among the three structural isomers, 6- and 8-hydroxylated metabolites were abundant in human urine, while 3-hydroxylated metabolites were hardly detectable, against the expectations from in vitro studies (Howard et al. 1990; Silvers et al. 1992; Chae et al. 1999). This demonstrated that 1-NP metabolism in humans is the same as that observed in in vivo studies. The measurement of urinary 1-NP metabolites was applied to taxi drivers' urine samples collected in China, and their concentrations were greater than metabolite levels previously reported in nonoccupationally exposed subjects (Miller-Schulze et al. 2013). The sum of urinary 1-NP metabolites was associated with personal exposure to 1-NP, and the results suggested that the metabolites reflect recent exposure (Galaviz et al. 2017).

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Part III
Emission Sources and Atmospheric Behavior

Chapter 5
Polycyclic Aromatic Hydrocarbons/Nitro-polycyclic Aromatic Hydrocarbons from Combustion Sources

Xiaoyang Yang and Kazuichi Hayakawa

Abstract PAHs/NPAHs are usually generated from diesel exhaust particulates (DEPs), coal burning-derived particulates (CBPs), and biomass burning exhaust particulates (BBPs). In order to describe the relative contributions of various sources and to make effective control strategies, accurate inventories are often conducted based on the strengths of emission activities and emission factors (EFs). Some reported EFs of PAHs and NPAHs from DEPs, CBPs, and BBPs are compared. The amount of PAHs generated is much smaller in DEPs than in CBPs or BBPs. In contrast, the EFs of NPAHs are higher in DEPs than those in CBPs and BBPs, respectively. This phenomenon is due to the much higher burning temperatures in diesel engine than those of coal or biomass burning. Therefore, the [1-NP]/[Pyr] ratio is selected as an indicator of the contribution of diesel-engine vehicles and coal combustion. Additionally, some isomer ratios of PAH and NPAH species are also shown.

Keywords Polycyclic aromatic hydrocarbons · Nitro-polycyclic aromatic hydrocarbons · Diesel exhaust particulates · Coal burning-derived particulates · Biomass burning · Exhaust particulates

In order to accurately assess the contributions of various combustion sources to atmospheric pollution and to human health risk, detailed characteristics of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) from different fuels are needed. PAHs/NPAHs are usually generated from diesel exhaust particulates (DEPs), coal burning-derived particulates (CBPs), and biomass burning exhaust particulates (BBPs). Domestic coal stoves or biomass stoves are popular direct combustion sources, especially during winter, for heating and cooking in suburban and

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rural areas of some developing countries (Chen et al. 2004a, b, 2005; Liu et al. 2009). A significant amount of this combustion takes place indoors with insufficient emission controls, and this results in serious indoor and outdoor air pollution (Chen et al. 2006; Zhi et al. 2008).

In order to describe the relative contributions of various sources and to make effective control strategies, accurate inventories are often conducted based on the strengths of emission activities and emission factors (EFs). Generally, EFs will vary depending on fuel category, fuel origin, burning instrumentation, combustion conditions, dilution technologies, and so on. Some reported EFs of PAHs and NPAHs from DEPs, CBPs, and BBPs are shown in Table 5.1. It can be seen that the PAH concentrations are much smaller in DEPs than in CBPs or BBPs. For example, total

Table 5.1 Concentrations of PAHs in DEP, CBP, and WBP (pmol mg^{-1})

	DEP		CBP		WBP
	Yang et al. (2010)	Tang et al. (2005)	Yang et al. (2010)	Tang et al. (2005)	Yang et al. (2010)
Nap	2.8 ± 4.8	–	ND	–	ND
Ace	5 ± 8.7	–	410 ± 720	–	43 ± 75
Fle	0.3 ± 0.5	–	910 ± 1400	–	2300 ± 3900
Phe	130 ± 120	–	4500 ± 3900	–	2600 ± 1600
Ant	ND	–	2300 ± 2200	–	580 ± 280
Flu	180 ± 82	180 ± 130	4200 ± 4000	400 ± 170	6600 ± 3700
Pyr	140 ± 200	180 ± 180	4200 ± 3500	350 ± 150	7500 ± 3800
BaA	11 ± 12	40 ± 30	1800 ± 950	90 ± 40	5300 ± 4400
Chr	27 ± 20	70 ± 40	1700 ± 1400	90 ± 80	7500 ± 7200
BbF	23 ± 21	30 ± 20	830 ± 1100	100 ± 90	4000 ± 5300
BkF	5 ± 7.8	10 ± 10	400 ± 280	20 ± 10	2400 ± 2900
BaP	0.61 ± 1.1	10 ± 10	950 ± 800	50 ± 30	6100 ± 7300
DBA	ND	–	ND	–	100 ± 180
BghiPe	8.8 ± 15	10 ± 10	500 ± 860	60 ± 30	3900 ± 3900
IDP	3.5 ± 5.7	10 ± 10	130 ± 190	30 ± 20	3400 ± 4400
Total	537 ± 499	540 ± 440	22,830 ± 21,300	1190 ± 620	52,323 ± 48,935
2-NF	110 ± 86	–	ND	–	0.7 ± 1.1
4-Nph	ND	–	0.7 ± 1.2	–	ND
9-Nph	ND	–	0.6 ± 0.9	–	0.5 ± 0.8
5-NAc	ND	–	ND	–	ND
2-NA	0.2 ± 0.2	–	0.8 ± 1.3	–	0.8 ± 1.3
9-NA	1.1 ± 1.9		0.2 ± 0.4		1.6 ± 2.7
1-NP	120 ± 28	65.5 ± 55.6	1.1 ± 0.7	1.43 ± 1.28	1.1 ± 1.8
2-NP	ND	–	ND	–	ND
4-NP	0.1 ± 0.2	–	0.6 ± 0.4	–	0.0 ± 0.1
3-NFR	1.9 ± 2.9	–	0.1 ± 0.2	–	0.0 ± 0.0
2-NTP	ND	–	ND	–	ND
7-NBaA	4.2 ± 4.9	–	0.06 ± 0.08	–	0.1 ± 0.2
6-NC	3.6 ± 6.2	–	0.4 ± 0.7	–	0.2 ± 0.3

(continued)

Table 5.1 (continued)

	DEP		CBP		WBP
	Yang et al. (2010)	Tang et al. (2005)	Yang et al. (2010)	Tang et al. (2005)	Yang et al. (2010)
3-NBA	18 ± 15	–	ND	–	ND
10-NBA	ND	–	ND	–	ND
1,3-DNP	0.7 ± 1.0	0.19 ± 0.19	0.01 ± 0.01	0.02 ± 0.03	0.2 ± 0.02
1,6-DNP	0.2 ± 0.2	0.16 ± 0.15	0.003 ± 0.003	0.05 ± 0.08	0.004 ± 0.007
1,8-DNP	0.5 ± 0.4	0.21 ± 0.19	0.06 ± 0.01	0.06 ± 0.05	0.04 ± 0.1
6-NBaP	0.6 ± 1.0	–	0.03 ± 0.003	–	0.02 ± 0.02
1-NPer	0.1 ± 0.2	–	ND	–	0.01 ± 0.01
3-NPer	2.2 ± 3.700	–	0.01 ± 0.02	–	0.01 ± 0.01
Total	263 ± 152	66.1 ± 56.1	4.7 ± 5.8	1.6 ± 1.4	5.2 ± 8.4

All data represent mean concentrations ± SD
ND Not detected

Table 5.2 PAH and NPAH diagnostic ratios for DEPs and CBPs

	DEPs	CBPs
Flu/(Flu + Pyr)	0.60–0.70	0.32–0.70
BaA/(BaA + Chr)	0.38–0.64	0.27–0.56
IND/(IND + BghiP)	0.35–0.70	0.23–0.63
BbF/(BbF + BkF)	0.75–0.82	0.60–0.89
1-NP/Pyr	0.36–0.86	0.0003–0.001

Data cited from Sicre et al. (1987), Oanh et al. (1999), Chen et al. (2005), Rogge et al. (1993), Tang et al. (2005), Shen et al. (2010, 2011) and Yang et al. (2010)

concentrations of 15 PAHs are 42.5 times and 97.4 times higher in CBPs and BBPs, respectively, than those in DEPs. However, NPAHs are about 60.0 times and 50.6 times higher in DEPs than in CBPs and BBPs, respectively. Since PAHs are formed at high temperatures and are partly nitrated in the presence of nitrogen oxides, the yield of NPAHs from the corresponding PAHs will increase with increasing temperature. Therefore, the yield of NPAHs from coal or wood stoves, which burn at around 900 °C, is smaller than that from diesel-engine vehicles, which run at 2700 °C. The above difference suggests that the ratio of a mono-NPAH to its parent PAH might be a useful indicator for the contribution of diesel-engine vehicles and coal combustion. Therefore, the [1-NP]/[Pyr] ratio is selected as an indicator of the contribution of diesel-engine vehicles and coal combustion (Table 5.2).

Additionally, a number of PAH isomer ratios, such as Flu/(Flu + Pyr), BaA/(BaA + Chr), IcdP/(IcdP + BghiP), BbF/(BbF + BkF), and BaP/(BaP + BghiP), are often used as source-specific indicators for PAH source apportionment (Watson 1984; Yunker et al. 2002; Galarneau 2008; Katsoyiannis et al. 2007; Ladji et al. 2009; Zhang et al. 2008). For example, it was reported that IcdP/(IcdP + BghiP) being larger than 0.5 indicated coal combustion and petroleum combustion if it is smaller than 0.5 (Yunker et al. 2002). Several frequently used PAHs diagnostic ratios and their general values in DEPs and CBPs are shown in Table 5.2.

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Chapter 6
Emission of Polycyclic Aromatic Hydrocarbons (PAHs) and Nitrated Polycyclic Aromatic Hydrocarbons (NPAHs) from Diesel Engines and Vehicles

Christopher D. Simpson

Abstract Diesel engine emissions are rich in PAHs and NPAHs, and vehicular emissions are a major source of PAHs and NPAHs in urban air. Specific NPAHs, including 1-nitropyrene, are enriched in diesel exhaust relative to other sources and have been used as source-specific tracers for diesel exhaust. However, changes in diesel engines and emission control technology driven by air quality regulations has led to substantial reductions in PAH and NPAH emissions from modern diesel engines and changes in the PAH/NPAH composition of these emissions. This chapter examines the contribution of diesel engine emissions to ambient PAH and NPAH concentrations and personal exposures and the effect of changing engine and exhaust treatment technologies on the PAHs and NPAHs emitted from diesel engines.

Keywords Diesel exhaust · Emissions control technology · 1-Nitropyrene

6.1 Introduction

Diesel engines are widely used to power vehicles in on-road and off-road applications, particularly in heavy-duty applications. Diesel engines are also used in combination with an electrical generator to provide electric power in places without connection to a power grid or as an emergency power supply if the grid fails. Relative to gasoline engines, diesel engines provide better fuel economy and greater durability (EPA 2002). However, older technology diesel engines have the disadvantage of emitting substantial amounts of hazardous air pollutants including oxides

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of nitrogen (NO_X), particulate matter, polycyclic aromatic hydrocarbons (PAHs), and nitro-PAHs (NPAHs) (IARC 2014). More stringent regulations on engine emissions have spurred advancements in diesel engine technology in the last 15–20 years, which have dramatically reduced the hazardous pollutant emissions from diesel engines. Emission control technology can also be retrofitted to older diesel engines to reduce levels of pollutants emitted. However, many diesel engines using older technology are still in use, and not all countries impose strict controls on vehicle emissions. Therefore, diesel engines continue to make a substantial contribution to ambient levels of PAHs and NPAHs – especially in urban areas (Tsai et al. 2004; Schulte et al. 2015; Di Vaio et al. 2016).

This article summarizes the current knowledge regarding PAH and NPAH emissions from contemporary diesel engines, including the contribution of diesel engine emissions to ambient concentrations of PAHs and NPAHs and the extent of human exposures to these compounds.

6.2 Diesel Exhaust Composition

Diesel exhaust is a complex mixture of gases and particles containing numerous known and suspected carcinogenic and mutagenic components. Particles are composed of elemental carbon, adsorbed organic compounds, and small amounts of sulfate, nitrate, metals, and other trace elements (Schauer et al. 1999). Gas phase constituents of concern include NO_X, carbon monoxide, and low molecular weight hydrocarbons, including aldehydes. Specific classes of chemicals in diesel exhaust that have received considerable attention include PAHs and NPAHs. NPAHs are considered to be a highly mutagenic class of compounds that are often formed by nitration reactions with PAHs either during combustion or during secondary photochemical reaction of primary emitted PAHs in the atmosphere (Arey et al. 1986; Bamford and Baker 2003; IARC 2014).

Specific NPAHs are enriched in diesel exhaust relative to other air pollution sources. For example, 1-nitropyrene (1-NP) has been proposed in numerous studies to be a source specific marker for diesel exhaust (Scheepers et al. 1995, 2003; Talaska et al. 1996). 1-NP is preferentially formed by the specific high temperature combustion processes in a diesel engine. This compound is the most abundant particle-associated NPAH observed in diesel exhaust particulate matter (DPM) (Scheepers and Bos 1992; Gallagher et al. 1994; Bezabeh et al. 2003). As shown in Fig. 6.1, the mass fraction of 1-NP is typically at least 40-fold higher in exhaust from older technology diesel engines compared to other common combustion sources. Bamford and colleagues examined the composition of NPAHs in DPM and urban air standard reference materials (SRMs) (Bamford et al. 2003; Bezabeh et al. 2003). They observed that 1-NP was the most abundant NPAH in the diesel SRMs, whereas 2-nitrofluoranthene (2-NF) was most abundant in the urban air SRMs. Three dinitropyrene isomers were only detected in the diesel SRMs.

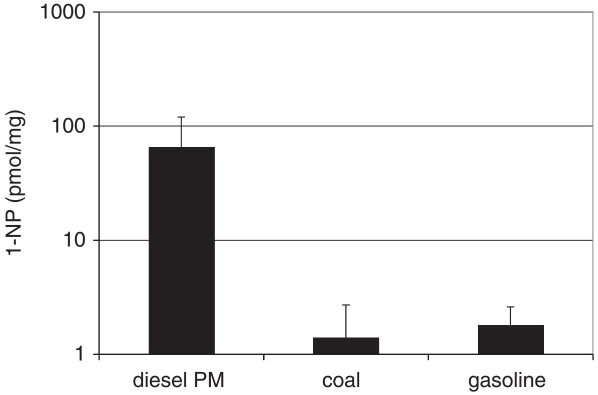

Fig. 6.1 Comparison of 1-NP mass fraction in various combustion sources (Data from Murahashi et al. 1995; Tang et al. 2005)

More recently, Hayakawa and colleagues have explored the ratios of specific NPAHs to their corresponding parent PAHs as indicators for the relative contribution of diesel exhaust to ambient NPAH concentrations (Hayakawa et al. 2014). They reported a 1-NP/pyrene ratio in diesel exhaust of 0.36, which is several orders of magnitude higher than the equivalent ratio in coal smoke and woodsmoke particles. The ratios of 6-nitrochrysene/chrysene, 7-nitrobenzo[a]anthracene/nitrobenzo[a]anthracene, and 6-nitrobenzo[a]pyrene/benzo[a]pyrene were similarly enriched in diesel exhaust.

However, it is important to note that while 1-NP is enriched in diesel emissions, it is not unique to diesel exhaust. 1-NP has also been detected to varying degrees in a variety of non-diesel combustion emissions including gasoline exhaust, coal smoke, woodsmoke, and kerosene heater emissions (Taga et al. 2005; IARC 2014).

The composition of diesel engine exhaust varies by engine type and condition, fuel, engine operation, and exhaust treatment such as particle filters and oxidation catalysts (McDonald et al. 2011; Alves et al. 2015). For example, ultralow-sulfur fuel (50 ppm sulfur) reduced PAH emissions from diesel buses by more than 90% compared to regular diesel fuel (500 ppm sulfur) (Lim et al. 2005).

Emissions are also influenced by engine operating conditions. Schuetzle and Perez (1983) reported that the emission rate of multiple NPAHs was higher under low load versus high load conditions. Similarly, Fox et al. (2015) reported a higher mass fraction of 1-NP in DPM formed under low versus high load conditions. In contrast the mass fraction (Fox et al. 2015) and the emission rate (Kweon et al. 2003) of particle-bound PAHs were higher under high load conditions compared to low load conditions.

6.3 DPM Control Technologies

As economic activity has increased globally, and particularly in East Asia, it has been accompanied by a concomitant increase in transportation, including diesel-powered vehicles (Hayakawa et al. 2014). As noted in earlier chapters of this book, diesel emissions have adverse impacts on human health and environmental quality. Consequently, governments have developed transportation policies and environmental regulations designed to help mitigate these negative impacts by improving the fuel economy and environmental performance of diesel engines. Figure 6.2 illustrates how particulate matter (PM) emission standards for heavy-duty vehicles have evolved in the European Union, the United States, Japan, and China from 1990 to 2015. As an example, in the United States, PM emission standards have dropped from 0.8 g/kWh in 1990 to 0.01 g/kWh in 2007 (Sharpe et al. 2011).

Typically a stepwise approach to improving engine emissions has been adopted, allowing engine manufacturers sufficient time to implement the technological advances necessary to meet the new emission standards (Miller and Facanha 2014).

While the rate of improvement in emission standards is impressive, typically these standards apply only to new diesel engines. The rapid reductions in allowable engine emissions, together with the long lifetime of a typical diesel engine, mean that in many cases emissions from diesel fleets are dominated by the emissions from older engines. For example, Zhang et al. (2015) note that in China pre-EURO and

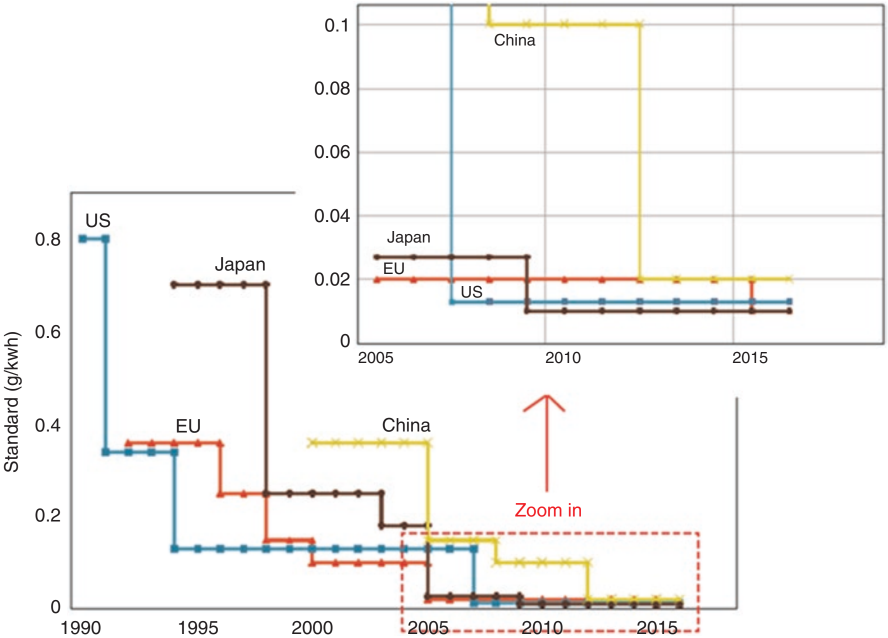

Fig. 6.2 PM standards for heavy-duty vehicles in the United States, the European Union, Japan, and China (Sharpe et al. 2011)

EURO 1 vehicles comprise only 42.8% of the total heavy-duty diesel vehicle population, yet they contribute 84.3% of the diesel vehicle PM emissions. In China, heavy-duty diesel trucks built before 2001 do not need to meet any engine standards, while those manufactured from 2001 to 2004 vehicles must meet national 1 emission standards for China, equivalent to the EURO 1 vehicle emission standard (Zhang et al. 2015). To accelerate reductions in emissions from in-use diesel vehicles, several agencies have implemented a variety of voluntary or mandatory engine retrofit programs. This includes the US Environmental Protection Agency's (USEPA) voluntary National Clean Diesel Campaign and the California Air Resources Board's mandatory Diesel Risk Reduction Plan (CARB 2000; USEPA 2016).

A range of emission control technologies have been implemented both on new diesel engines and as retrofits for older in-use diesel engines. The main technologies used to reduce PM emissions are diesel oxidation catalysts (DOC), diesel particulate filters (DPF), and closed crankcase ventilation (MECA 2007; IARC 2014). In addition, exhaust gas recirculation (EGR) and selective catalytic reduction (SCR) technologies may be employed to reduce emissions of NO_x. In general, these technologies also substantially reduce PAH and NPAH emissions (Heeb et al. 2008, 2010; Hu et al. 2013; Khalek et al. 2015). Khalek et al. (2015) tested emissions from three heavy-duty diesel engines equipped with DOC, DPF, SCR, and an ammonia slip catalyst and were fueled with ultralow-sulfur diesel fuel (~6.5 ppm sulfur). These engines were compliant with 2010 USEPA NO_X emission standards and had emissions of PAHs and NPAHs that were 90 to >99% lower than pre-2007 model engines. Emissions of these compounds from the 2010 engines were also substantially lower than emissions from 2007 technology engines (Fig. 6.3) (Khalek et al. 2015).

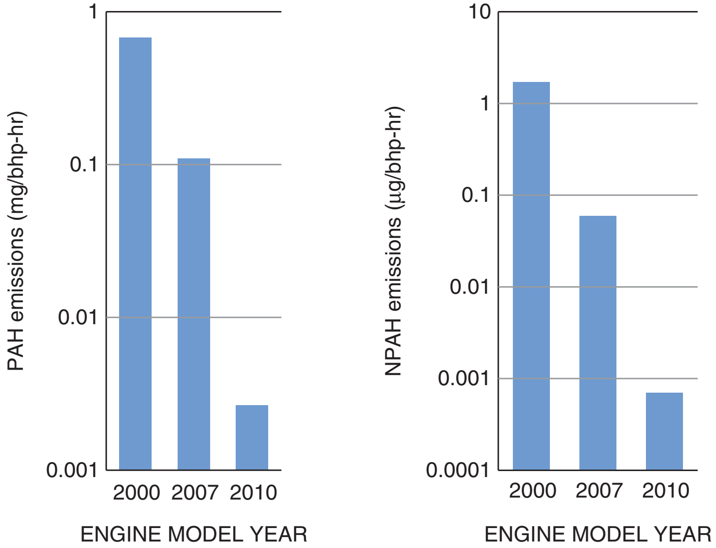

Fig. 6.3 Improvements in PAH and NPAH emissions with new diesel engine technologies (Adapted from Khalek et al. 2015)

However, there have been examples where specific exhaust treatment methods have actually increased emissions of specific NPAH compounds (Sharp et al. 2000; Heeb et al. 2008, 2010; Hu et al. 2013). For example, Heeb et al. (2008) reported that a cordierite-based monolithic wall-flow DPF reduced PAH emissions and aromatic hydrocarbon (AH) receptor agonist activity. Emissions of four- and five-ring NPAHS were also reduced with the DPF; however, emissions of specific two- and three-ring NPAHS were increased. The authors concluded that selective nitration of the corresponding parent PAHs was occurring in the DPF. A subsequent study in 2010, investigating a variety of DPFs including versions with high oxidation potential and versions with low oxidation potential, largely confirmed the findings of the 2008 study (Heeb et al. 2010). Sharp et al. (2000) observed that 1-NP emissions increased but 2-NF emissions decreased when diesel exhaust was treated with an oxidation catalyst, whereas Hu et al. (2013) reported reductions in 1-NP but increases in 3- and 9-nitrophenanthrene for various exhaust treatments including DPF and SCR.

In general, the replacement of conventional diesel fuel with various biodiesel blends has reduced emissions of both PAHs and NPAHs (Bagley et al. 1998; Sharp et al. 2000). Bagley et al. (1998) observed 65–85% reductions in PAH emissions from biodiesel compared to conventional diesel fuel. Similarly, Sharpe et al. (2000) reported that biodiesel reduced NPAH emissions by 50–90% compared to conventional diesel fuel.

Closed crankcase ventilation technology is also likely to reduce emissions of PAHs: PAHs were detected in both crankcase and tailpipe emissions from two diesel school buses, whereas 1-NP was only detected in the tailpipe emissions (Zielinska et al. 2008). In contrast, Manabe et al. (1984) reported high levels of 1-NP in used crankcase oil (138 μg/L of oil).

6.4 Diesel Exhaust Contributions to Ambient PAH and NPAH Concentrations and Personal Exposures

The highest exposures to diesel exhaust are often encountered in occupational settings. For example, exposures to DPM in underground mines have been reported in the range between 5 and 500 $\mu g/m^3$ (measured as elemental carbon (EC), whereas ambient exposures to DPM rarely exceeded a few tens of $\mu g/m^3$ (Vermeulen et al. 2010; IARC 2014; Schulte et al. 2015). Similarly, high levels of 1-NP (up to 5 ng/m^3) have been detected in underground mines (Scheepers et al. 1995, 2003; Seidel et al. 2002). In 2006 the US Mine Safety and Health Administration (MSHA) elected to control DPM exposures by setting the permissible exposure limit (PEL) in metal/nonmetal mines at 160 $\mu g/m^3$ (measured as total carbon). In order to meet the PEL, many mine operators had to retrofit their existing in-use diesel engines with emission control technologies (Riley et al. 2017). Subsequently a study conducted in one mine in the United States, after implementation of the MSHA PEL, reported much lower concentrations of both EC and 1-NP (geometric mean (GM) for 1-NP of 0.06 ng/m^3 and GM of 12 μg/m^3 EC) for underground miners in active ore extraction tasks (range, 0.002–0.5 ng/m^3) (Riley et al. 2017) The lower DPM concentrations observed in this latter study were attributed to the use of biodiesel blend fuel and retrofitting of diesel engines with catalyzed DPFs.

Vehicular emissions are among the most important anthropogenic sources of PAHs in urban air (Lim et al. 2005; Alkurdi et al. 2013; Di Vaio et al. 2016). Considering ambient NPAH concentrations, after 2-NF, 1-NP is the most abundant of 28 mononitro- and dinitro-PAHs identified in airborne PM (Bamford et al. 2003). 2-NF is formed primarily as a secondary pollutant through photochemical reactions (Arey et al. 1986; Bamford and Baker 2003), whereas the most important source of 1-NP is from traffic emissions and in particular from diesel engines (Arey et al. 1986; Bamford et al. 2003). Photochemical formation in the atmosphere was reported for 2-nitropyrene, but not for 1-NP (Arey et al. 1986). Using a combination of source testing and environmental measurements, Kakimoto et al. (2000) estimated that >99% of 1-NP in three Japanese cities was derived from diesel exhaust. Hayakawa et al. (2014) used ratios of specific nitro-PAHs to their corresponding parent PAHs as markers for the contribution of diesel exhaust to ambient NPAH concentrations. Using this approach they concluded that diesel exhaust was the major source of NPAHs in the Japanese and Korean cities they studied, whereas coal was the major source of atmospheric NPAHs in China (Hayakawa et al. 2014). In addition to the NPAHs emitted as primary pollutants from diesel engines, diesel emissions are also a major source of PAHs, several of which undergo photochemical reactions to produce NPAHs (Arey et al. 1986; Ramdahl et al. 1986).

More recently, Schulte et al. (2015) used land use regression modeling of 1-NP concentrations to examine neighborhood scale spatial variability in diesel exhaust concentrations in an urban community. They found that 1-NP concentrations were strongly associated with diesel-specific land use characteristics such as proximity to railroads and local truck pollution emission estimates.

6.5 Conclusion

Historically, diesel engines and vehicles have been an important source of ambient concentrations and personal exposures to a variety of PAHs and NPAHs. For specific NPAHs, notably 1-NP, diesel exhaust has been the predominant source of those compounds. In many countries advancements in diesel engine technology – often driven by government regulations aimed at improving air quality – have led to diesel engines with dramatically reduced emissions of PAHs and NPAHs. However, many countries have transportation policies that allow for the continued use of older model diesel engines, and the operating lifetime of a diesel engine may be several decades. As a result, it will be many years before the full environmental benefits of new low-emission diesel engines are realized. In the meantime we are in a transition period where the magnitude of PAH and NPAH emissions from diesel engines and the composition of the diesel emissions themselves are changing rapidly.

While the projected reductions in PAH and NPAH emissions are undoubtedly beneficial for the environment and for human health overall, these changes will also create new challenges for researchers who study PAHs and NPAHs and their association with diesel exhaust and human health. For example, while 1-NP has to date proven to be a helpful source tracer for DPM and a surrogate for DPM exposures, as 1-NP emissions from diesel engines decrease, the proportion of 1-NP exposures from non-diesel sources will increase. Ultimately this may diminish the utility of 1-NP as a surrogate for DPM. Similarly, the changing composition of diesel emissions has already been shown to elicit different toxicological profiles in vitro and in animal studies. This likely translates into changing the toxicological potency and risk estimates of fleet-aggregated diesel emissions, which will create additional challenges for epidemiological studies – especially studies of chronic diseases linked to diesel exhaust exposure such as lung cancer and cardiovascular disease.

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Chapter 7
Atmospheric Reactions of PAH Derivatives: Formation and Degradation

Takayuki Kameda

Abstract Polycyclic aromatic compounds are ubiquitous atmospheric pollutants with toxic, mutagenic, and carcinogenic properties. They are produced from the chemical reactions of their parent or related compounds in the atmosphere as well as from a wide variety of anthropogenic sources, such as fuel combustion. In this chapter, chemical reaction pathways for the atmospheric secondary formation of several polycyclic aromatic hydrocarbon (PAH) derivatives, i.e., gas-phase formation of mutagenic 1- and 2-nitrotriphenylene via OH or NO_3 radical-initiated reactions of the parent triphenylene, formation of carcinogenic 1-nitropyrene from heterogeneous nitration of pyrene on mineral dust aerosols, atmospheric formation of hydroxynitropyrenes from a photochemical reaction of 1-nitropyrene, and photochemical degradation of selected nitrated and oxygenated PAHs on airborne particles under simulated solar UV irradiation, are addressed.

Keywords Polycyclic aromatic compounds · Secondary formation · Photoreaction · Heterogeneous reaction · Gas-phase reaction

7.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (e.g., nitrated, oxygenated, and hydroxylated derivatives: NPAHs, OPAHs, and OHPAHs) are ubiquitous atmospheric pollutants with toxic, mutagenic, and carcinogenic properties (Salmeen et al. 1984; Schuetzle 1983). These compounds are produced from a wide variety of anthropogenic sources such as the incomplete combustion of fossil fuels used in industrial plants, through heating, and in diesel-powered vehicles (Schuetzle et al. 1982; Bamford et al. 2003; Bezabeh et al. 2003). NPAHs, which generally exhibit higher mutagenicity and carcinogenicity than their parent PAHs, are also generated from atmospheric reactions of PAHs released in the gas phase with

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radical species such as OH and NO_3 radicals and nitrogen oxides (Atkinson and Arey 1994; Ciccioli et al. 1996; Reisen and Arey 2005; Sasaki et al. 1997; Zielinska et al. 1989). OPAHs and OHPAHs, which may show biological effects beyond mutagenicity and carcinogenicity, are also known to be formed secondarily via oxidation of PAHs and NPAHs in the atmosphere (Cvrčková et al. 2006; Warner et al. 2004). These PAH derivatives generally have lower volatility than the parent PAHs. As a result, they are more likely to be deposited on airborne particles, especially fine particles which are easily suspended in the atmosphere and can easily be inhaled into the human body. Thus, it is necessary to understand the secondary formation processes of PAH derivatives in order to fully understand their effects on humans. In this chapter, chemical reaction pathways for the secondary formation of PAH derivatives are addressed.

7.2 Formation of Nitrotriphenylenes by Radical-Initiated Reactions

As described above, several types of NPAHs are formed via gas-phase reactions of semi-volatile PAHs. For example, 2-nitropyrene (2-NP) is formed by the gas-phase reaction of pyrene with OH radicals in the presence of NO_2, and 2-nitrofluoranthene (2-NFR) is formed by OH or NO_3 radical-initiated reactions of fluoranthene in the gas phase (Atkinson and Arey 1994). Benzanthrone, which has very low vapor pressure, was also found to react with radical species and NO_2 to yield a nitrated compound in the gas phase (Phousongphouang and Arey 2003). Nitrotriphenylenes (NTPs), which include the strongly mutagenic isomer 2-nitrotriphenylene (2-NTP), have been found in airborne particles as well (Ishii, et al. 2000, 2001; Kameda et al. 2004; Kawanaka et al. 2005). The possibility of the atmospheric formation of NTPs via reactions of triphenylene was based on seasonal and diurnal changes in the concentration of ambient NTPs (Ishii et al. 2001; Kameda et al. 2004). Because the strongly mutagenic 2-NTP has been found in air at concentrations comparable to those of 1-nitropyrene (1-NP) and 2-NFR, which are the most abundant airborne NPAHs (Ishii, et al. 2000, 2001; Kameda et al. 2004; Kawanaka et al. 2005), the contribution of 2-NTP to the mutagenicity of airborne particles may be significant. From the point of view of public hygiene, it is important to acquire more detailed data about the environmental occurrence of NTPs. Thus, the formation of 1-nitrotriphenylene (1-NTP) and 2-NTP by gas-phase OH or NO_3 radical-initiated reactions of triphenylene was demonstrated using a flow reaction system (Kameda et al. 2006). Nitration of triphenylene with N_2O_5 in CCl_4 was also examined in order to determine the isomer distributions of NTPs formed via the NO_3 radical-initiated nitration of triphenylene and in order to predict the rate constants of the gas-phase OH or NO_3 radical-initiated reactions of triphenylene.

The formation of 1- and 2-NTP was clearly shown by HPLC analysis of the products of the gas-phase reaction of triphenylene initiated by OH radicals. A

2-NTP/1-NTP ratio of 1.22 was obtained for OH radical-initiated nitration. In contrast, the NO_3 radical-initiated reaction predominantly gave 2-NTP, with traces of 1-NTP. Because the amount of 1-NTP formed in the NO_3 radical-initiated reaction was too small to determine, a precise 2-NTP/1-NTP value could not be calculated and was thus assumed to be a value greater than 1.5. The preferential production of 2-NTP was also observed in the nitration of triphenylene with N_2O_5 in CCl_4, for which the yields of 1- and 2-NTP were 6 (±2) % and 35 (±2) %, respectively. It has been reported that the reactions of several kinds of PAH with N_2O_5 in CCl_4 are similar in terms of nitro-isomer distribution to gas-phase NO_3 radical-initiated nitration (Phousongphouang and Arey 2003; Zielinska et al. 1986). Thus, the analogous isomer distribution of NTP (the larger yield of 2-NTP over 1-NTP) in the gas-phase reaction to that in CCl_4 liquid-phase nitration does not contradict previous findings regarding the nitration of PAHs. The mean 2-NTP/1-NTP ratio in samples of airborne particles was >1.55. This value was similar to the ratios from the radical-initiated reactions and was much higher than that of the diesel exhaust particulate (DEP) samples (2-NTP/1-NTP = 0.37). This indicates that the atmospheric radical-initiated reactions significantly contribute to the formation of airborne NTPs, especially 2-NTP. The gas-phase formation of NPAHs via OH or NO_3 radical-initiated reactions involves the addition of an OH or NO_3 radical to the PAH at the carbon atom with the highest electron density, followed by ortho-addition of NO_2. This is followed by a loss of water or nitric acid. For triphenylene, the carbon at the 1-position is the most electron-rich (Barker et al. 1955; Radner 1983); therefore, preferential formation of 2-NTP over 1-NTP is expected in the gas-phase radical-initiated reaction (Fig. 7.1).

The rate constants of gas-phase reactions of triphenylene with OH and NO_3 radicals at 298 K were predicted to be $(8.6 \pm 1.2) \times 10^{-12}$ $cm^3 molecule^{-1}$ s^{-1} and $(6.6 \pm 1.5) \times 10^{-29}$ $[NO_2]$ cm^3 $molecule^{-1}$ s^{-1}, respectively, using a relative-rate method in a CCl_4 liquid-phase system (Kameda et al. 2013). Based on the ambient concentrations of 2-NTP and the rate constant obtained for the reaction of triphenylene with the radicals, the atmospheric loss rate of 2-NTP relative to 2-NFR (which is the most abundant NPAH and is also produced from radical reactions) was successfully estimated. That is to say, 2-NTP is less susceptible to decomposition than 2-NFR, under ambient conditions.

7.3 Secondary Formation of 1-Nitropyrene Promoted on Mineral Dust Aerosols

One of the most abundant NPAHs is 1-NP, which is formed through the combustion of fossil fuels such as coal and diesel fuel (Schuetzle 1983; Yang et al. 2010). 1-NP is likely a carcinogen (IARC 2013) and can also be formed from gas-particle phase heterogeneous reactions (Esteve et al. 2004; Finlayson-Pitts and Pitts 2000; Inazu et al. 2000; Miet et al. 2009; Nguyen et al. 2009; Ramdahl et al. 1984; Wang et al.

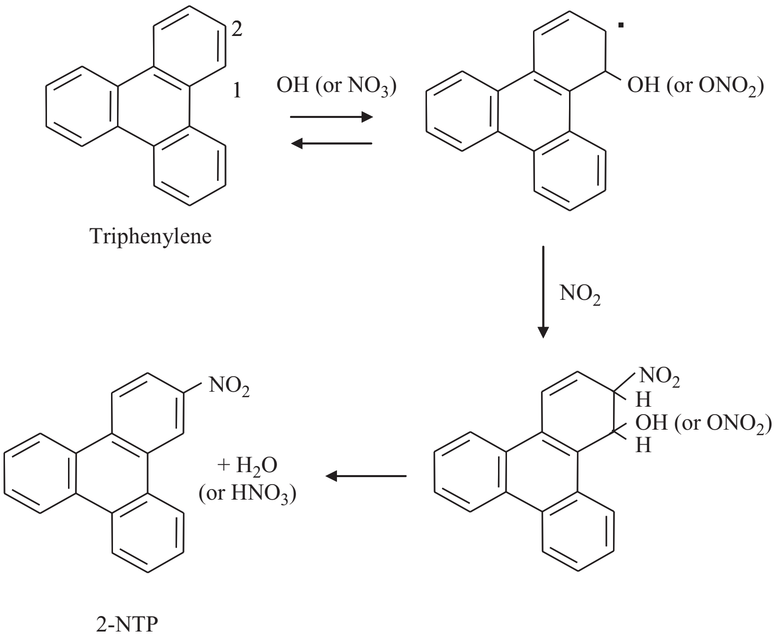


Fig. 7.1 A schematic for the formation of 2-NTP from OH or NO_3 radical-initiated reactions of triphenylene (Kameda 2011). (Reproduced with permission from Journal of Health Science Vol. 57 No. 6. Copyright 2011 The Pharmaceutical Society of Japan)

2000). It is formed by the reaction of pyrene (Py) with gaseous NO_2 on various substrates such as graphite, as a model for soot (Esteve et al. 2004), and a variety of metal oxides, as models for mineral aerosols (Inazu et al. 2000; Miet et al. 2009; Ramdahl et al. 1984; Wang et al. 2000). However, the heterogeneous formation of atmospheric 1-NP has been previously thought to be negligible because the reaction rate and the yield of 1-NP through this process are not sufficient to account for ambient 1-NP concentration (Finlayson-Pitts and Pitts 2000; Nguyen et al. 2009; Ramdahl et al. 1984; Shiraiwa et al. 2009). Previous studies of heterogeneous NPAH formation used simple inorganic oxides such as SiO_2, Al_2O_3, and TiO_2 as models of mineral dust aerosols (Inazu et al. 2000; Ma et al. 2011; Wang et al. 2000), but these substances lack the complexity of real mineral dust aerosols and thus may not be good models for investigating heterogeneous NPAH formation. Mineral dust is a major component of airborne particulates on a global scale (Cwiertny et al. 2008). It is transported by wind from deserts or semiarid regions (Tanaka and Chiba 2006), which account for 40% of the total world land area (Fernández 2002). Organic compounds adsorbed on the surface of mineral dust can have important health implications (Falkovich et al. 2004). Thus, the formation of 1-NP from Py and NO_2 on authentic mineral dust was examined (Kameda et al. 2016).

In the NO_2 exposure experiments of particle-bound Py, degradation of Py was measured under 3 ppmv NO_2 air in the dark. On quartz (SiO_2) particles, Py was

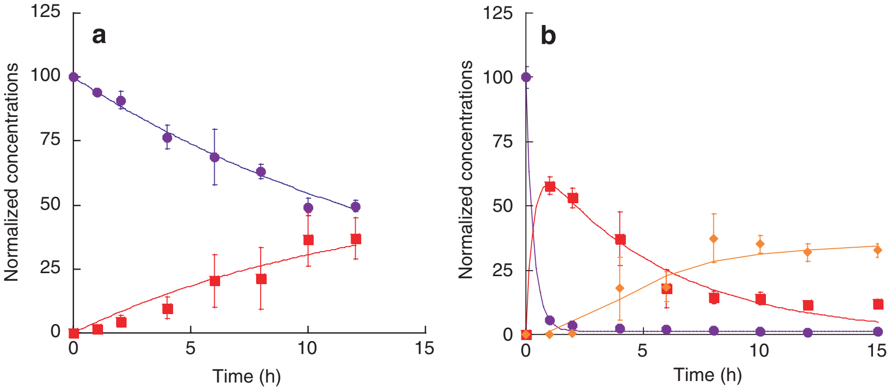


Fig. 7.2 Concentrations of Py and nitropyrenes (1-NP and DNPs) on quartz (**a**) and CDD (**b**) (expressed as a percent of the initial Py concentration) after exposure to 3 ppmv NO_2 for the indicated times (Reproduced from Kameda et al. 2016). The data points represent mean values (± 1 SD) of triplicate experiments: circles, Py; squares, 1-NP; diamonds, DNPs (= 1,3-DNP + 1,6-DNP + 1,8-DNP). The curves for Py decay are exponential nonlinear least-square fits assuming first-order reactions. The curves for nitropyrene formation are for illustrative purposes only

slowly converted to 1-NP, reaching a yield of ~40% in 12 h (Fig. 7.2a). On Chinese desert dust (CDD) particles, more than 90% of the initial amount of Py was degraded, and the maximum yield of 1-NP was attained after a reaction time of 1 h (Fig. 7.2b). 1-NP was then gradually converted to dinitropyrenes (DNPs) (Fig. 7.2b). Other mononitropyrene isomers were not detected. Desert dust is generally composed of various minerals including quartz, corundum (α-Al_2O_3), clay minerals, carbonates, feldspars, and hematite (Fe_2O_3) (Usher et al. 2003). To determine which components contribute to rapid nitration, the percentage of degraded Py (D_{Py}) and the yield of 1-NP ($Y_{1\text{-NP}}$) were compared during a reaction time of 2 h on various substrates that generally constitute desert dust. The most active components were natural montmorillonites, kaolin, and saponite, as well as Arizona test dust (ATD; standard test dust made from Arizona desert sand) and CDD (Table 7.1). In most of these cases, the conversion of Py to 1-NP was completed within 2 h (Table 7.1). DNP formation was observed except on saponite. Kaolin, montmorillonites A and B, and saponite are types of clay minerals. For the other mineral substrates, such as quartz, carbonates (limestone and dolomite), and feldspars, D_{Py} and $Y_{1\text{-NP}}$ were less than 20%, and no DNP was formed during the NO_2 exposure (Table 7.1). To quantify the rate of degradation of Py on each substrate, the kinetics of the heterogeneous reaction between NO_2 and Py adsorbed on the substrates tested in this study were determined by following the consumption of Py as a function of NO_2 exposure time. The apparent rate constants of the pseudo-first-order reaction, k_{obs}, were (2.9×10^{-4} to 2.5×10^{-3}) s^{-1} on CDD, ATD, and clay minerals and (2.5×10^{-6} to 9.0×10^{-5}) s^{-1} on the other substrates when the concentration of NO_2 was 3 ppmv.

The nitration of PAHs is catalyzed by acids (Shiri et al. 2010). Thus, the surface acid property of mineral dust may play a role in the heterogeneous nitration of Py.

Table 7.1 Observed pseudo-first order rate constants for the reaction of Py on the substrates examined in this study with 3 ppmv NO_2 (k_{obs}), percentage of degraded Py (D_{Py}), and yields of 1-NP ($Y_{1\text{-NP}}$)

Substrates	$k_{obs} \times 10^5$ (s^{-1})[a]	D_{Py} (%)[b]	$Y_{1\text{-NP}}$ (%)[b]	DNP formation[c]
Chinese desert dust (CDD)	86 ± 4	96	53	+
Arizona test dust (ATD)	36 ± 1	88	58	+
Kaolin[d]	110 ± 10	98	60	+
Montmorillonite A	53 ± 5	95	89	+
Montmorillonite B	29 ± 4	84	79	+
Saponite	39 ± 3	82	73	–
Potassium feldspar	1.1 ± 0.2	14	10	–
Sodium feldspar	0.30 ± 0.06	12	6	–
Feldspar	0.86 ± 0.14	17	4	–
Limestone	1.4 ± 0.1	18	5	–
Dolomite	0.83 ± 0.15	16	4	–
Calcium sulfate	1.5 ± 0.5	6	0	–
Quartz	1.7 ± 0.1	9	5	–
Aluminum oxide	0.25 ± 0.00	2	1	–
Iron (III) oxide	9.0 ± 3.3	17	0	–
Titanium (IV) oxide	1.4 ± 0.0	14	3	–
Montmorillonite K10[e]	250 ± 20	100	6	+
Graphite[f]	1.9 ± 0.1	9	1	–

Reproduced from Kameda et al. (2016)

[a] Errors represent one standard error derived from nonlinear least-squares fitting for the Py decay plots

[b] Obtained from reactions for 2 h

[c] Reaction time, 12 h; +, yes; –, no

[d] Note that kaolin consists largely of kaolinite

[e] Acid-activated montmorillonite

[f] As a control

The surface acid properties of solid catalysts, including clay minerals, can be examined using Fourier transform infrared spectroscopy (FT-IR) with pyridine as a probe (Parry 1963). When pyridine binds to Brønsted acid sites, pyridinium ions are produced, which have an absorption band around 1545 cm^{-1}. In contrast, pyridine molecules coordinated to Lewis acid sites have an absorption band around 1445 cm^{-1}. The band at 1490 cm^{-1} is attributed to both molecules. The spectra of pyridine adsorbed onto some substrates (CDD, ATD, montmorillonites, kaolin, and saponite) have absorption bands at (1445 and 1490) cm^{-1}, while no absorption band is observed around 1545 cm^{-1}, except in the cases of kaolin and montmorillonite K10 (Fig. 7.3). This suggests that CDD and ATD, as well as clay minerals, have abundant acid sites, particularly Lewis acid sites. On the contrary, the spectra of the other substrates displayed no clear peaks, indicating that they have little to no acid sites on their surfaces. The largest k_{obs} value was obtained for the reaction on montmorillonite K10, an acid-activated clay. These results strongly suggest that

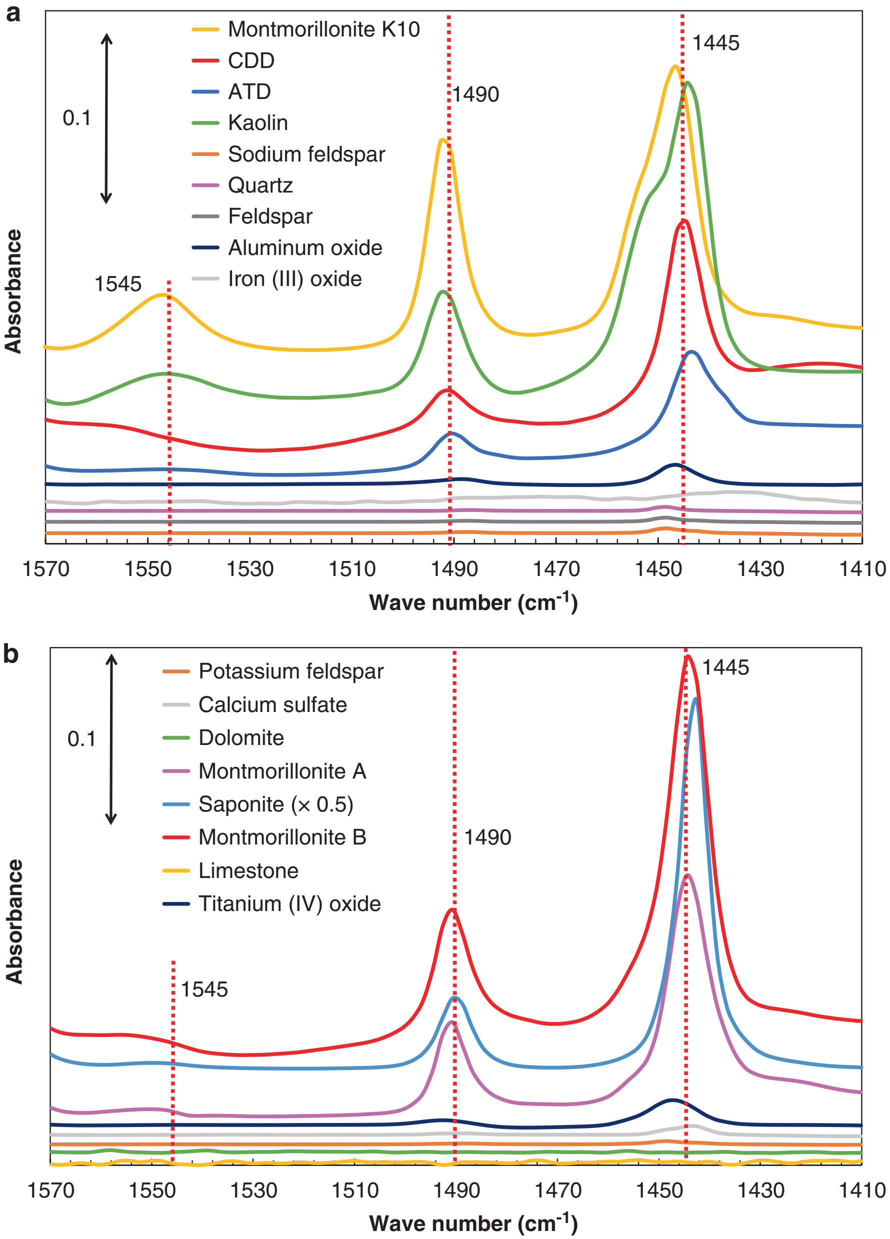
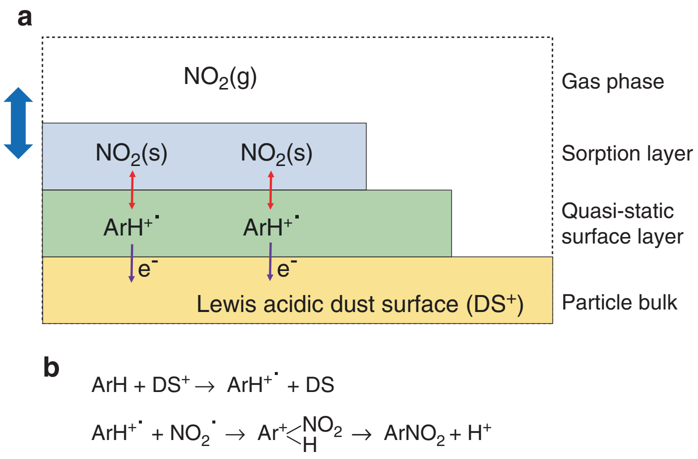


Fig. 7.3 IR spectra of pyridine adsorbed on the substrates examined in the study (Reproduced from Kameda et al. 2016)

substrates showing acidic surface properties have an accelerating effect on the rate of heterogeneous nitration of PAHs by NO_2.

Lewis acid sites on aluminosilicates are proposed to function as electron acceptors, leading to the formation of aromatic radical cations *via* electron transfer (Laszlo 1987; Soma and Soma 1989). The radical cations of several kinds of PAHs, such as Py, perylene, anthracene, and benzo[*a*]pyrene (which form on the surface of aluminosilicates), have been identified by spectroscopic methods, such as electron spin resonance (ESR) (Garcia and Roth 2002). These cations would couple with surface NO_2 to yield NPAHs (Laszlo 1987), similar to that with the nitrous acid-catalyzed (NAC) nitration mechanism (Ridd 1991). That is, the rate-determining step would be the subsequent addition of NO_2 to the aromatic radical cation yielding a σ complex (Wheland intermediate), and the deprotonation of this complex would constitute the final fast step that produces the nitrocompound (Fig. 7.4). Thus, the finding that the Lewis acid property of the substrates probably plays a role in nitration suggests that the rapid formation of 1-NP on mineral dust is the result of NO_2 reacting with the radical cations of Py, which form at the surface Lewis acid sites (Fig.7.4).



$$ArH + DS^+ \rightarrow ArH^{+\bullet} + DS$$

$$ArH^{+\bullet} + NO_2^{\bullet} \rightarrow Ar^+{<}^{NO_2}_{H} \rightarrow ArNO_2 + H^+$$

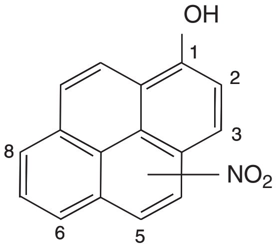
Fig. 7.4 Proposed mechanisms for the nitration of aromatic compounds (ArH) on the acidic surface of mineral dust (Reproduced from Kameda et al. 2016). (**a**) Schematic illustration of the heterogeneous nitration. The gas-particle interface is divided into a gas-phase with gaseous NO_2 ($NO_2(g)$), a sorption layer with adsorbed NO_2 ($NO_2(s)$), a quasi-static surface layer with the aromatic radical cation ($ArH^{+\bullet}$), and a particle bulk. The blue arrow indicates the adsorption and desorption fluxes of NO_2. The red and purple arrows indicate chemical reactions and electron transfer, respectively. This heterogeneous chemistry is based on the Pöschl-Rudich-Ammann (PRA) framework (Shiraiwa et al. 2009). (**b**) Chemical reaction scheme of the nitroaromatic compound ($ArNO_2$) formation on Lewis acid sites of the dust surface (DS^+)

7.4 Atmospheric Formation of Hydroxynitropyrenes from a Photochemical Reaction of Particle-Associated 1-Nitropyrene

The 1-NP taken up by humans and animals is transformed into various metabolites such as hydroxynitropyrenes (OHNPs), in the presence of cytochrome P450 enzymes (Rosser et al. 1996). Several isomers of OHNP (Fig. 7.5), such as 1-hydroxy-3-nitropyrene (1-OH-3-NP), 1-hydroxy-6-nitropyrene (1-OH-6-NP), and 1-hydroxy-8-nitropyrene (1-OH-8-NP), have also been observed on airborne particles (Gibson et al. 1986; Kameda et al. 2010) and on diesel exhaust particles (DEP) (Manabe et al. 1985; Schuetzle 1983; Schuetzle et al. 1985). Several studies have found that most OHNP isomers have lower mutagenic activity than the parent 1-NP (Ball et al. 1984; Rosser et al. 1996; Manabe et al. 1985). Recently, however, OHNPs such as 1-OH-3-NP, 1-OH-6-NP, and 1-OH-8-NP have been found to act as endocrine disruptors: they act as estrogenic, anti-estrogenic, and anti-androgenic compounds (Kameda et al. 2008, 2011a) that may cause dysfunction of human and wildlife endocrine systems, abnormal development of reproductive systems, and immunodeficiencies. In view of the influence of OHNPs on human health, we need to learn more about their environmental concentration levels, sources, and behaviors. Therefore, the formation of OHNPs including 1-OH-3-NP, 1-OH-6-NP, and 1-OH-8-NP from photochemical reactions of 1-NP was examined in laboratory experiments to clarify the occurrence of atmospheric OHNPs (Kameda et al. 2011b).

Figure 7.6 shows a profile of an HPLC analysis using chemiluminescence detection (HPLC/CLD) for the products from photoreactions of 1-NP in methanol. Five chromatographic peaks were observed in the chromatogram (symbolized as A, B, C, D, and E). The retention times of peaks B, C, D, and E were the same as those of authentic 1-OH-6-NP, 1-OH-8-NP, 1-OH-3-NP, and 1-OH-2-NP, respectively. When analyzed by LC/MS/MS, a fraction containing the photoreaction products also yielded five peaks. By comparing the retention times and the MS/MS spectra of these peaks with those of the authentic standards, four known OHNPs (1-OH-2-NP, 1-OH-3-NP, 1-OH-6-NP, and 1-OH-8-NP) were identified. For these compounds, the molecule-related ion *m/z* 262 ([M-H]$^-$) together with the characteristic fragment ions *m/z* 232 ([M-H-NO]$^-$) and 216 ([M-H-NO$_2$]$^-$) was detected in a full scan analysis. In the study, and for the first time, 1-OH-3-NP, 1-OH-6-NP, and 1-OH-8-NP were found in 1-NP photoreaction products. The unknown compound that was

Fig. 7.5 Structure of hydroxynitropyrene



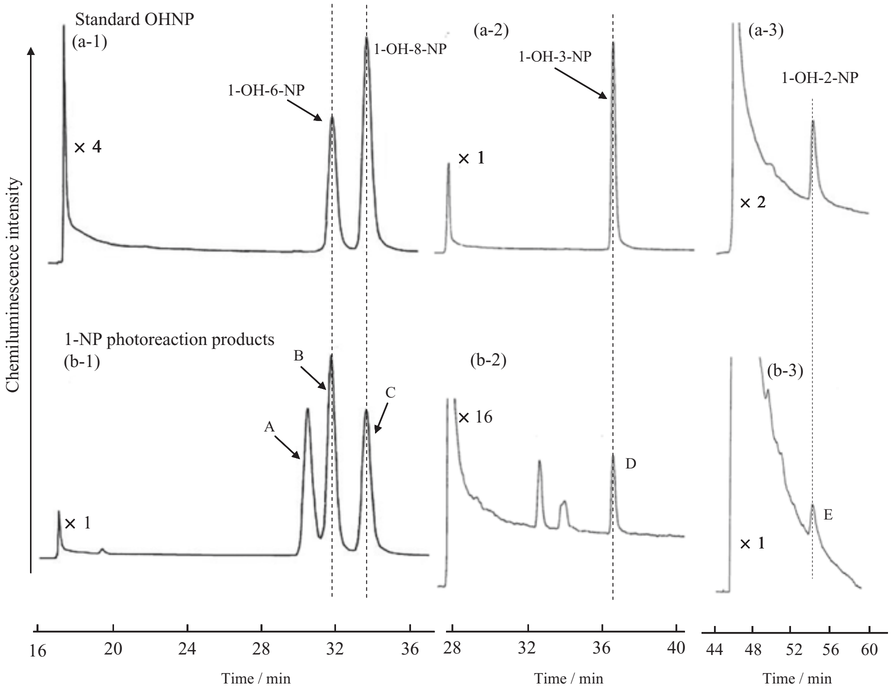


Fig. 7.6 Chromatograms of standard OHNPs (**a**) and photoreaction products of 1-NP (**b**) obtained by the HPLC-chemiluminescence detection system (Kameda 2011) (Reproduced with permission from Journal of Health Science Vol. 57 No. 6. Copyright 2011 The Pharmaceutical Society of Japan)

observed in the HPLC/CLD chromatogram was also observed in the LC/MS/MS analysis. This compound also gave a characteristic MS/MS spectrum with a molecule-related ion *m/z* 262 and fragment ions *m/z* 232 and *m/z* 216. The similarity between the fragmentation patterns of the unknown compound and known OHNPs indicates that the unknown compound is an isomer of OHNP. The structure of the unknown compound obtained by the preparative scale photoreaction was then determined by analysis of its ^{1}H–NMR spectrum. On the basis of chemical shifts and coupling patterns, the unknown compound contained in the photo-reaction products was identified as 1-hydroxy-5-nitropyrene (1-OH-5-NP).

All the OHNP isomers, which were found in the 1-NP photoreaction products, were also identified in ambient airborne particles collected at a typical residential area in Osaka, Japan. In contrast, 1-OH-2-NP and 1-OH-5-NP were not found in Standard Reference Materials (SRM) 1650b and SRM 1975, which are typical DEP samples. The concentrations of the other OHNP isomers in the DEP samples were much lower than the concentration of 1-NP. On the other hand, significantly higher concentration ratios of ΣOHNP (= 1-OH-3-NP + 1-OH-6-NP + 1-OH-8-NP) to 1-NP were observed in ambient airborne particles rather than in the DEP samples. In ambient airborne particles, the mean ΣOHNP/1-NP concentration ratio of 1.4 was 35 times higher than that in SRM 1650b and 470 times higher than that in SRM 1975. The diurnal concentration of 1-NP observed at the site in Osaka increased early in the morning and late in the evening, suggesting that automotive emissions contributed to the occurrence of 1-NP. The OHNP concentrations also rose in the morning, and variations of OHNP concentrations similar to those of 1-NP were observed during the daytime. However, the concentrations of OHNPs did not increase during the evening rush hour and were low at night (i.e., in the absence of sunlight). These results support the idea that atmospheric OHNPs are predominantly formed *via* secondary formation processes; photochemical reactions of 1-NP are expected to have a significant effect on the occurrence of OHNPs in the atmosphere.

7.5 Photochemical Decomposition of Selected Nitro- and Oxy-polycyclic Aromatic Hydrocarbons on Airborne Particles Under Simulated Solar UV Irradiation

As in the case of 1-NP, photo-induced decomposition is a dominant pathway for the degradation of particle-associated PAH derivatives (Finlayson-Pitts and Pitts 2000; Kamens et al. 1988). Solar radiation in the UV spectral region can modify PAH derivatives to form new compounds that may exhibit different types of biological effects. These might include the disruption of endocrine systems and the production of reactive oxygen species (ROS) in the human body (Chung et al. 2007). Thus, it is necessary to understand the photodecomposition of PAH derivatives in order to understand their effects on humans. However, the rate constants and the quantum yields related to the photolysis of the derivatized PAHs, which are the most significant factors for photodecomposition, have not been studied well. Thus, photodecomposition experiments for selected OPAHs and NPAHs, including 3-nitrobenzanthrone (3-NBA) a nitrated aromatic ketone that is strongly mutagenic (Enya et al. 1997), were conducted on a glass surface. With this as a simple model of airborne particles, the photolysis rate constants and the quantum yields for the PAH derivatives in the system were determined (Kameda et al. 2009). Furthermore, the atmospheric lifetime of the compounds due to photodecomposition was estimated using the actinic flux on the Earth's surface, photolysis rate constants, and quantum yields obtained in the study.

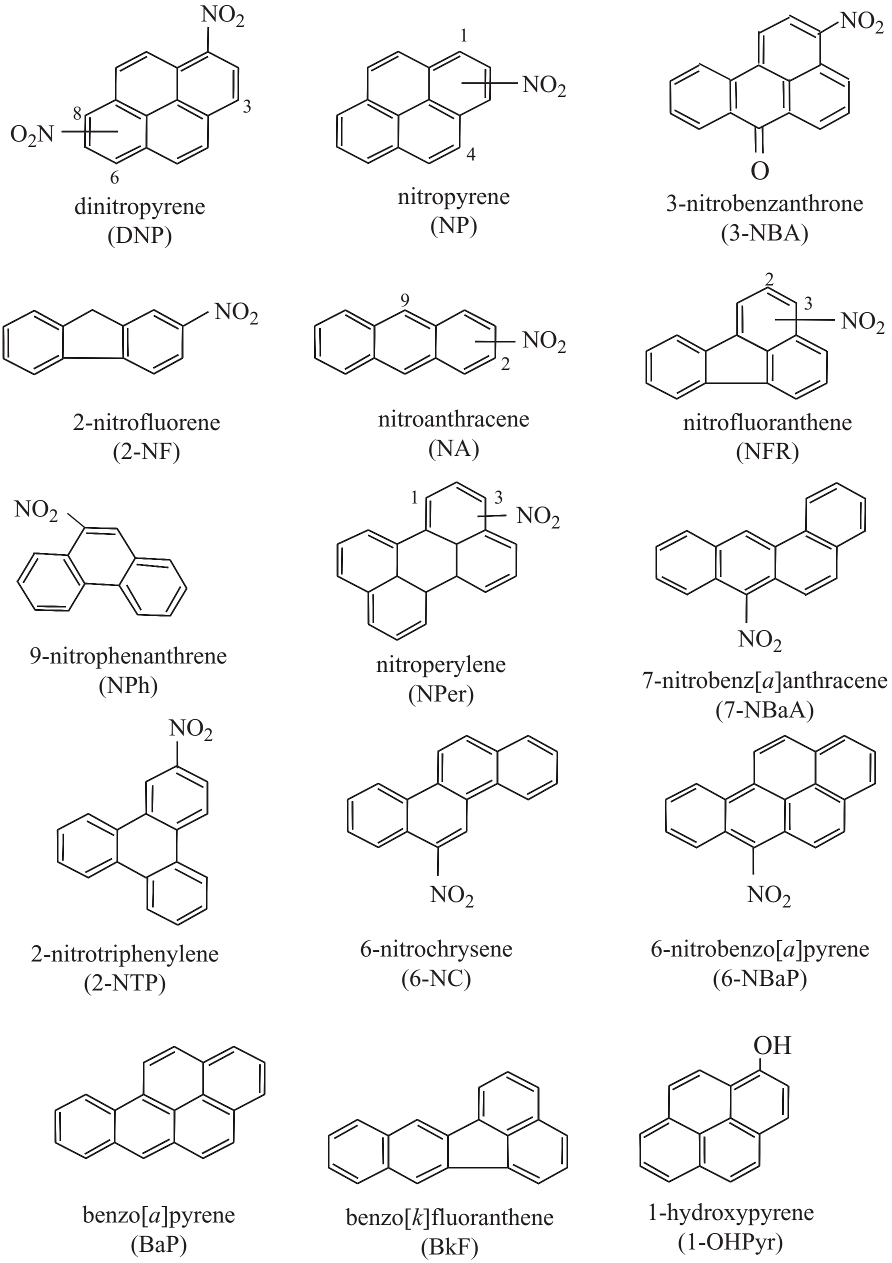
The highest photolysis rate constant was observed for 9-nitroanthracene (9-NA), while 4-nitropyrene (4-NP) and 3-NBA were found to be the most stable of the nitrated compounds under UV irradiation (Table 7.2). It is hypothesized that photoreactivity of NPAHs is governed by the orientation of the nitro group; i.e., NPAHs having nitro groups perpendicular to the aromatic ring are more easily photodecomposed than those having parallel ones (Yang et al. 1994; Warner et al. 2004). The fast photodegradations observed for 9-NA, 6-nitrobenzo[*a*]pyrene (6-NBaP), and 7-nitrobenz[*a*]anthracene (7-NBaA), which all have a perpendicular nitro group, were consistent with this hypothesis (Fig. 7.7). The photoreaction products of

Table 7.2 Quantum yield, photolysis rate constant, and estimated lifetime of the PAH derivatives on the Earth's surface

Compound	Photolysis rate constant (s^{-1})	Lifetime (h)
BaP	2.22×10^{-5}	74.6
BkF	9.89×10^{-6}	125.3
1-OHPyr	2.38×10^{-4}	9.3
1,3-DNP	8.15×10^{-5}	15.3
1,6-DNP	1.75×10^{-4}	7.6
1,8-DNP	2.23×10^{-4}	5.8
1-NP	7.85×10^{-5}	17.8
1-NPer	1.42×10^{-3}	1.0
2-NA	1.01×10^{-3}	1.6
2-NF	3.26×10^{-4}	6.6
2-NFR	1.05×10^{-4}	17.4
2-NTP	1.02×10^{-4}	21.1
3-NBA	5.23×10^{-5}	22.2
3-NFR	8.56×10^{-5}	17.8
3-NPer	1.65×10^{-4}	9.9
4-NP	7.31×10^{-5}	21.5
6-NBaP	1.38×10^{-3}	1.0
6-NC	5.93×10^{-4}	2.8
7-NBaA	2.12×10^{-3}	0.9
9-NA	3.15×10^{-3}	0.5
9-NPh	4.79×10^{-4}	4.3
1,2-BAQ	4.74×10^{-5}	34.9
1,4-CQ	7.63×10^{-5}	15.8
5,6-CQ	9.86×10^{-5}	11.6
9,10-PQ	2.23×10^{-4}	7.1
AcQ	2.35×10^{-4}	7.0
AQ	8.38×10^{-5}	22.7
B[c]P-5,6-Q	4.33×10^{-4}	4.5

Reproduced in part from Kameda et al. (2009), See Fig. 7.7 for compound abbreviations

NPAHs were reported to include quinoid PAHs (Warner et al. 2004), as well as photoreaction products of PAHs. Benzo[*c*]phenanthrene-5,6-quinone (BcP-5,6-Q), which has a similar photolysis rate constant to 9-nitrophenanthrene (9-NPh), degraded the fastest of the seven OPAHs tested. Of all the substituted PAHs examined in the study, 1,2-benzanthraquinone (1,2-BAQ) was most resistant to photodecomposition. Although previous studies on the photostability of OPAHs were quite limited, Cvrčková and Ciganek (2005) reported that 9,10-phenanthraquinone (9,10-PQ) was less stable than anthraquinone (AQ) under UV irradiation. This is consistent with the results.



dinitropyrene (DNP)

nitropyrene (NP)

3-nitrobenzanthrone (3-NBA)

2-nitrofluorene (2-NF)

nitroanthracene (NA)

nitrofluoranthene (NFR)

9-nitrophenanthrene (NPh)

nitroperylene (NPer)

7-nitrobenz[*a*]anthracene (7-NBaA)

2-nitrotriphenylene (2-NTP)

6-nitrochrysene (6-NC)

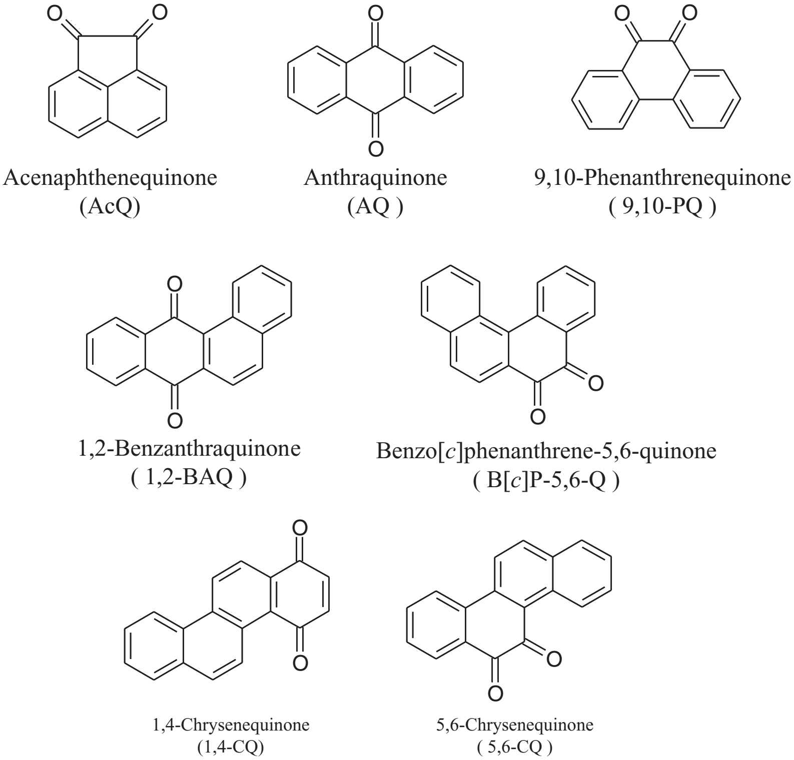
6-nitrobenzo[*a*]pyrene (6-NBaP)

benzo[*a*]pyrene (BaP)

benzo[*k*]fluoranthene (BkF)

1-hydroxypyrene (1-OHPyr)

Fig. 7.7 Structures of PAH derivatives examined in the photodecomposition experiment



Acenaphthenequinone
(AcQ)

Anthraquinone
(AQ)

9,10-Phenanthrenequinone
(9,10-PQ)

1,2-Benzanthraquinone
(1,2-BAQ)

Benzo[*c*]phenanthrene-5,6-quinone
(B[*c*]P-5,6-Q)

1,4-Chrysenequinone
(1,4-CQ)

5,6-Chrysenequinone
(5,6-CQ)

Fig. 7.7 (continued)

The photolysis rate constants of the compounds tested under solar irradiation were estimated based on the actinic flux at the Earth’s surface (Demerjian et al. 1980) and on the quantum yields obtained in the study. Atmospheric lifetimes of the compounds due to photodecomposition were calculated to be 0.5–22 h for NPAHs and 4.5–35 h for OPAHs using the obtained photolysis rate constants. OPAHs were found to be more stable against photo-irradiation than were NPAHs. This indicates that the risk induced by OPAHs is critical for human health, because we may be continuously exposed to OPAHs due to their longer residence time in the atmosphere. Recently, it has been found that ROS, which can cause severe oxidative stress connected with inflammatory processes, is produced in larger amounts via chain reactions induced by quinoid PAHs in the human body (Chung et al. 2007). Further studies on the biological effects and on the atmospheric formation and decomposition mechanisms of OPAHs are required.

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Part IV

Atmospheric Polycyclic Aromatic Hydrocarbons and PM2.5

Chapter 8

Recent Trends in Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Japanese Cities

Kazuichi Hayakawa

Abstract Total suspended particulate matter (TSP) was collected during the summer and winter in Japanese cities (Sapporo, Kanazawa, Tokyo, Sagamihara, and Kitakyushu) from 1997 to 2014. Polycyclic aromatic hydrocarbons (PAHs) with four to six rings and two nitropolycyclic aromatic hydrocarbons (NPAHs), 1-nitropyrene and 6-nitrobenzo[*a*]pyrene, were determined. A comparison between PAH and NPAH concentrations and [NPAH]/[PAH] ratios revealed the following characteristics:

1. Commercial cities (Sapporo, Kanazawa, Tokyo, and Sagamihara): the concentrations of PAHs and NPAHs were high at the beginning of the sampling period and then steadily decreased, with NPAHs decreasing more than PAHs. The major contributor was automobiles, but their contributions decreased significantly as a result of the effective regulation control of particulate matter and NO_x emitted from automobiles.
2. Iron-manufacturing cities (Kitakyushu and Muroran): PAH concentrations did not decrease, though concentrations of NPAHs decreased. The major contributor of PAHs was iron manufacturing which uses a large amount of coal.

Keywords Polycyclic aromatic hydrocarbons · Nitropolycyclic aromatic hydrocarbons · Japanese urban atmospheric pollution · Recent pollution trends · Emission source

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8.1 Introduction

In the 1970s and 1980s, urban air pollution in Japanese cities became serious, and automobiles were considered to be the major contributor with many kinds of pollutants such as carbon dioxide, sulfur oxides, nitrogen oxides, polycyclic aromatic hydrocarbons (PAHs), and nitropolycyclic aromatic hydrocarbons (NPAHs). Automobiles were identified as the main source of atmospheric PAHs and NPAHs in Kanazawa, a commercial city in Japan, as seen by the parallel between variations in diurnal PAH and NPAH concentrations and traffic volume (Fig. 8.1) (Hayakawa et al. 1995; Murahashi et al. 1995). The Japanese government gradually reinforced controls on nitrogen oxides (NO_x) and PM emitted from automobiles starting in the 1990s (Ministry of Land, Infrastructure Transport and Tourism 2017). As a result, a decrease in PAH and NPAH concentrations was observed (Kojima et al. 2010; Hama et al. 2012; Suzuki et al. 2015; Inomata et al. 2016). In this chapter, the changes in atmospheric concentrations and sources of PAHs and NPAHs during the period from 1997 to 2014 were clarified to obtain a more accurate picture of the effect of government emission controls on the allowable emissions from automobiles.

Total suspended particulate matter (TSP) was collected in Sapporo, Kanazawa, Tokyo, Sagamihara, and Kitakyushu (Fig. 8.2). Sapporo and Kanazawa, the respective capital cities of Hokkaido and Ishikawa Prefecture, are commercial cities though the former has a population about five times larger. Tokyo, having the largest population, is the capital of Japan, and Sagamihara is a typical satellite city of Tokyo. Both are commercial cities. Kitakyushu is one of the major iron-manufacturing cities in Japan. TSP samples in each city were collected for 2 weeks in winter (January–February) and summer (July–August) by using high-volume air

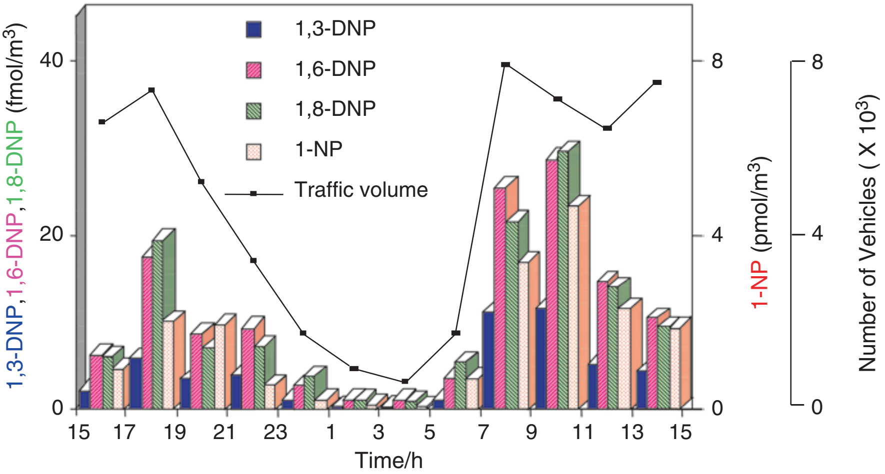
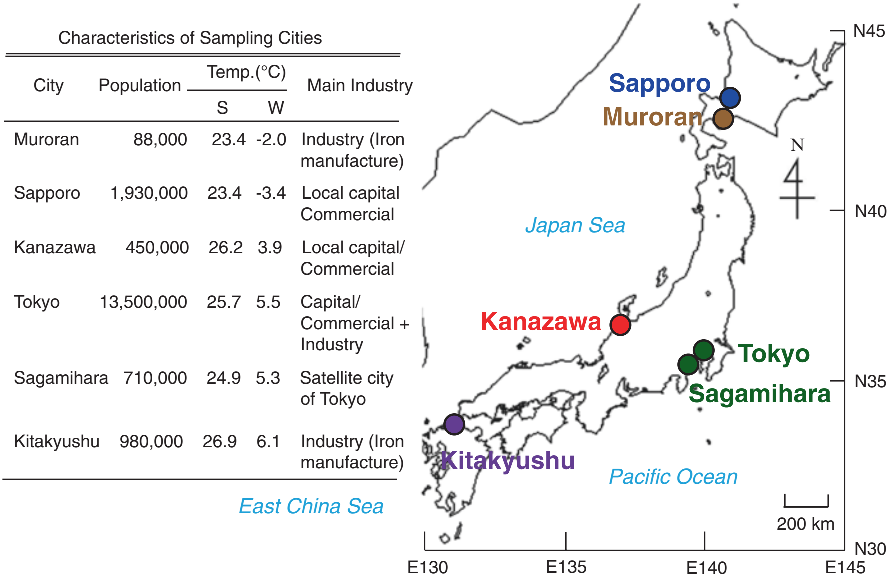


Fig. 8.1 Diurnal variations of 1,3-, 1,6-, and 1,8-dinitropyrenes (DNPs) and 1-NP in urban air sampling site of downtown Kanazawa; sampling period: February 2–3, 1993



Characteristics of Sampling Cities

City	Population	Temp.(°C)		Main Industry
		S	W	
Muroran	88,000	23.4	-2.0	Industry (Iron manufacture)
Sapporo	1,930,000	23.4	-3.4	Local capital Commercial
Kanazawa	450,000	26.2	3.9	Local capital/ Commercial
Tokyo	13,500,000	25.7	5.5	Capital/ Commercial + Industry
Sagamihara	710,000	24.9	5.3	Satellite city of Tokyo
Kitakyushu	980,000	26.9	6.1	Industry (Iron manufacture)

Fig. 8.2 Airborne particulate sampling cities in Japan

samplers. Nine PAHs, fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, benzo[*ghi*]perylene (BghiPe), and indeno[1,2,3-*cd*]pyrene (IDP), were determined by using an HPLC equipped with a fluorescence detector. Two NPAHs, 1-nitropyrene (1-NP) and 6-nitrobenz[a]pyrene (6-NBaP), were determined using an HPLC equipped with a fluorescence detector.

8.2 Long-Term Changes in PAH and NPAH Concentrations from 1997 to 2014

In Sapporo, Kanazawa, and Tokyo, the highest mean ΣPAH concentrations observed were in the range between 5.1 and 8.0 ng/m^3 in winter 1997 or 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the respective concentrations decreased to 1/6 (summer), 1/3 (winter) and 1/3 (summer), and 1/2 (winter) of the initial concentrations with seasonal differences (winter > summer). However, TSP concentrations did not show any statistical decrease in these cities. In Kitakyushu, the initial mean ΣPAH concentrations (3.0 ng/m^3 in summer 1997 and 4.6 ng/m^3 in winter 1997) were at the levels similar to those of the other Japanese cities and remained at similar levels until a sudden increase in 2014, despite a low TSP concentration (Hayakawa et al. 2017). The variations in BaP, as a representative PAH, in the five cities are shown in Fig. 8.3. In Sapporo, Kanazawa, and Tokyo, the highest mean

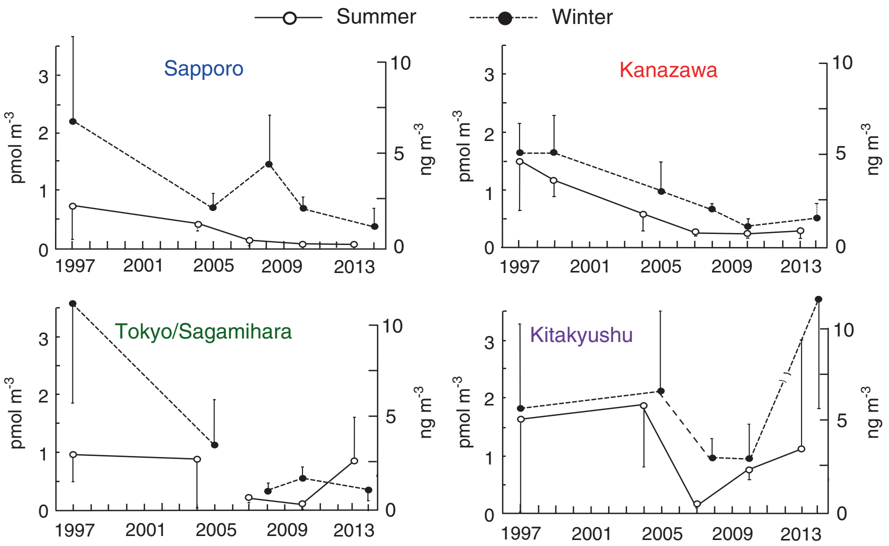


Fig. 8.3 Atmospheric BaP concentrations

BaP concentrations observed were in the range between 0.48 and 0.91 ng/m^3 in the winter of 1997 or 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the concentrations decreased significantly with seasonal differences (winter > summer). In Kitakyushu, the initial BaP concentrations (0.40 ng/m^3 in summer 1997 and 0.45 ng/m^3 in winter 1997) were at the levels similar to those of the other Japanese cities and increased suddenly to 1.72 ng/m^3 in winter 2014.

In Sapporo, Kanazawa, and Tokyo, the highest winter ΣNPAH concentrations ranged from 70 to 141 pg/m^3 and were observed during the winters of 1997 and 1999. Subsequently, in Sapporo, Kanazawa, and Tokyo, the concentrations decreased more significantly than those of PAHs. The rates of decrease were faster in the first stage (during 1997–2005) than in the second stage (2007–2014). However, Kitakyushu showed different patterns. The initial mean ΣNPAH concentrations in summer and winter were much lower than those of the other three Japanese cities. The subsequent summer concentration seemed to decrease, but the winter concentration did not (Hayakawa et al. 2017). Variations in 1-NP, as a representative NPAH, in the five cities are shown in Fig. 8.4. In Sapporo, Kanazawa, and Tokyo, the highest winter 1-NP concentrations ranged from 70 to 141 pg/m^3 and were observed in winter 1997. Subsequently, the concentrations decreased more significantly than those of BaP and faster in the first stage (during 1997–2005) than in the second stage (2007–2014). However, Kitakyushu showed initial mean 1-NP concentrations in both summer and winter that were much lower than those of the other three Japanese cities. While the summer concentration seemed to subsequently decrease, the winter concentration did not.

Figures 8.3 and 8.4 showed that air pollution caused by PAHs and NPAHs has improved in Sapporo, Kanazawa, and Tokyo, especially in the first stage but not in

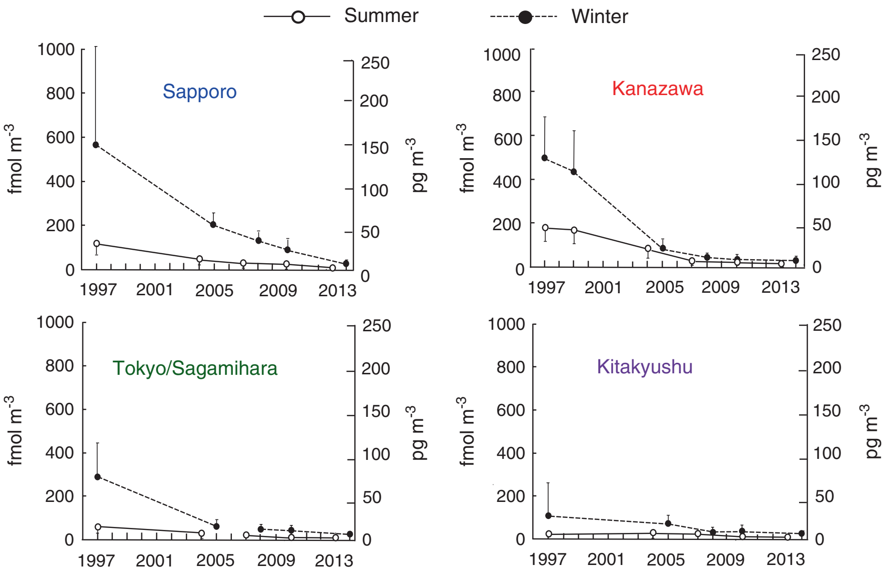


Fig. 8.4 Atmospheric 1-NP concentrations

Kitakyushu. The most important difference between Japanese cities and the other Far Eastern Asian countries is that pollution levels of PAHs and NPAHs in China and Far Eastern Russia were much higher than those in Japan by 1–2 orders of magnitude or more (Tang et al. 2002, 2005; Hattori et al. 2007).

8.3 Source Estimation

We previously reported that the concentration ratio of NPAH to corresponding PAH ([NPAH]/[PAH]) in TSP becomes larger with an increase in combustion temperature (Tang et al. 2005; Hama et al. 2012). This is because the formation of NO_2 and the mono- and di-nitration of PAHs depends on the combustion temperature. Depending on the combustion temperature and differences between coal-burning stoves (1100–1200 °C) and automobile engines (2700–3000 °C), the [1-NP]/[Pyr] value of PM from coal stoves ($8 \times 10^{-4} - 6 \times 10^{-3}$) was much smaller than that of PM from automobile engines (0.36) as seen in Fig. 8.5 (Yang et al. 2010).

The diurnal variations in atmospheric PAH and NPAH concentrations were in parallel with traffic volume in Kanazawa, a typical local commercial city in Japan (Hayakawa et al. 1995), suggesting automobiles were the main contributors (Hama et al. 2012). Figure 8.6 shows changes in [1-NP]/[Pyr] ratios for the five Japanese cities from 1997 to 2014 with a single value for Muroran in winter 2009. At the beginning of the study, Kanazawa showed the largest summer and winter [1-NP]/[Pyr] ratios (0.18 and 0.20, respectively). From the average [1-NP]/[Pyr] ratio (0.35)

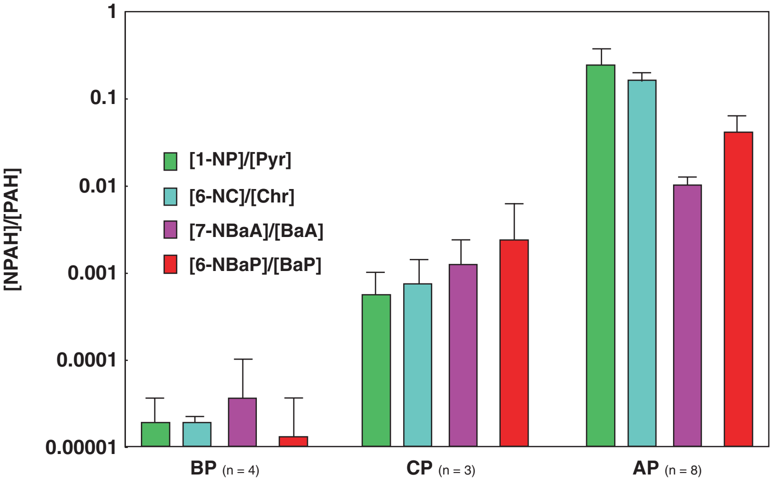


Fig. 8.5 [NPAH]/[PAH] ratios of automobile engine exhaust particulates (AP), coal-burning particulates (CP), and biomass-burning particulates (BP)

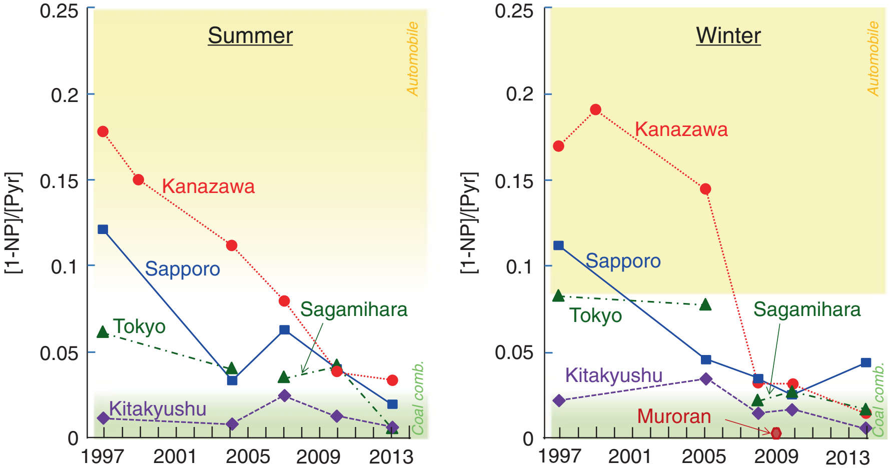


Fig. 8.6 Variation in [1-NP]/[Pyr] ratios

of PM exhausted from diesel engines, the contribution of automobiles to atmospheric PAHs and NPAHs was calculated to be between 47 and 57%. These values decreased significantly to 0.03 ($p < 0.01$) and 0.013 ($p < 0.01$), respectively, in 2013/2014.

Sapporo showed the largest [1-NP]/[Pyr] ratios (0.12 in both summer and winter) in 1997. They decreased to 0.019 and 0.043 ($p < 0.01$) by 2013/2014. The recent small [1-NP]/[Pyr] ratios suggest that the contribution of automobiles decreased significantly.

8.4 The Effect of Regulations on Atmospheric PAH/NPAH Levels

In Japan, during the period between 1995 and 2014, the registered number of cars increased from 44,680,000 to 60,670,000, while the registered number of trucks/buses, which consisted mainly of diesel-engine vehicles, decreased from 20,670,000 to 14,850,000. This alone does not explain the significant decreases in atmospheric NPAH concentrations shown in Fig. 8.4. Automobile mileage was also improved through innovations in engine performance and oil quality (Japan Automobile Manufacturers Association 2017). This might be another reason. Recently, the Japanese government enforced legislation limiting the values of NO_x and PM from new diesel vehicles through a step-by-step procedure starting in 1993. Emissions of CO, HC, and NO_x from new gasoline car in 2000, 2001, and 2002 (Shin-tanki kisei) were similarly restricted. Figure 8.7 shows the change of the regulation values of NO_x and PM emitted from new diesel vehicles of three weight categories, < 1.7 tons, 1.7–3.5 tons, and >3.5 tons, as an example of automobile categories. The regulation values of NO_x and PM from diesel-engine automobiles (≦ 3.5 tons) decreased significantly to 13.7–29.4% and 2.8–3.8% of the original levels before 1997. Because TSP contains not only PM exhausted from automobiles but also soils and particulates from the road surface, the decreases in Pyr and BaP may be explained primarily by decreases in regulation values of PM from automobiles (Fig. 8.7). Considering that the formation of NPAHs depends on [PM] and [NO_2], it is reasonable that atmospheric concentrations of 1-NP and 6-NBaP decreased faster than

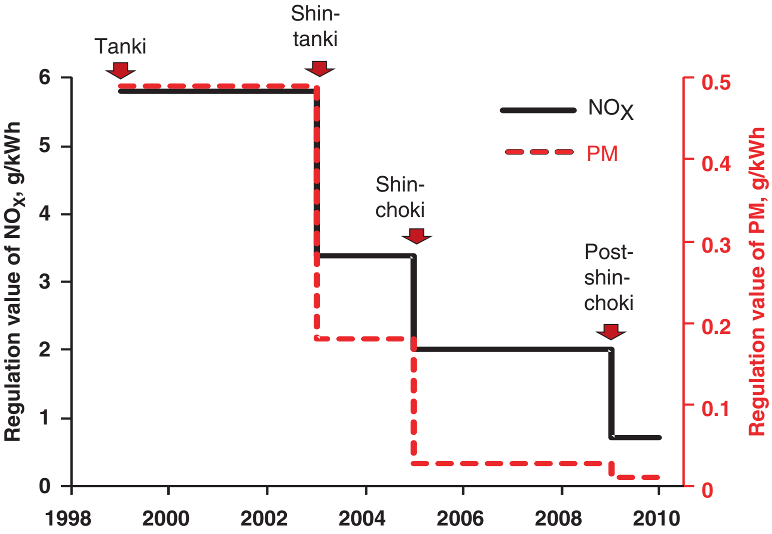


Fig. 8.7 Japanese regulation of NO_X and PM emissions from new diesel-engine vehicle regulation names: Tanki, short-term; Shin-tanki, new short-term; Shin-choki, new long-term; Post shin-tanki, post new short-term

those of Pyr and BaP, respectively. The rapid decrease in atmospheric concentrations of PAHs and NPAHs (Figs. 8.3 and 8.4) means that governmental control of PM and NO_x emission from automobiles has dramatically improved urban air pollution caused by automobiles in Japanese commercial cities (Kakimoto et al. 2000, 2002; Kashiwakura et al. 2008, 2009).

By contrast, Kitakyushu showed a different [1-NP]/[Pyr] profile. The values were very low during the monitoring period. The values were below 0.0004 in 2013/2014 (Fig. 8.6). Similarly, in another recent study of Muroran, which is a typical iron-manufacturing city in Japan, the [1-NP]/[Pyr] ratio was also very small (3.1×10^{-3}) in the winter of 2009. A coke-oven iron-manufacturing plant, which consumes a large amount of coal, was found to be the major contributor of PAHs in the city (Hayakawa et al. 2016). Like Muroran, Kitakyushu is also a major iron-manufacturing city.

8.5 Conclusion

An analysis of long-term concentrations of atmospheric PAHs and NPAHs, as well as [NPAH]/[PAH] ratios in five Japanese cities from Hokkaido to Kyushu from 1997 to 2014, led to two conclusions:

1. Commercial cities [Sapporo, Kanazawa, Tokyo, and Sagamihara]: the concentrations of PAHs and NPAHs were high in the 1990s and then decreased. NPAHs decreased faster than PAHs. The major source was automobiles at the beginning, but the contribution of automobiles decreased significantly after the enforcement of regulations aimed at curbing automobile emissions.
2. Iron-manufacturing cities [Kitakyushu and Muroran]: the concentrations of PAHs did not decrease, while the concentrations of NPAHs decreased. The major PAH contributor was from iron manufacturing.

From the comparison of Japanese cities (Chap. 8) and the other East Asian countries (Chap. 9), it must be emphasized that the pollution levels of PAHs and NPAHs in Japanese urban air were much lower than those in China and Russia and that the major sources are different. Automobiles are the major contributor in Japanese commercial cities such as Sapporo, Tokyo, Kanazawa, and Busan. While iron manufacturing, which consumes a large amount of coal, is the major contributor in Kitakyushu and Muroran, winter coal heating is the major contributor in Shenyang, Beijing, and Vladivostok. In the automobile cities, the concentration of NPAHs relative to the concentration of PAHs was higher in East Asian countries. This means that there will be differences between locales that require differing countermeasures (Hayakawa 2016).

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Chapter 9
PAHs/NPAHs in Northeast Asia

Ning Tang

Abstract Airborne particulates were collected in 13 cities in Northeast Asia in winter and summer from 1997 to 2010. Polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) in the extracts from the particulates were analyzed using HPLC with fluorescence and chemiluminescence detection, respectively. Both PAH and NPAH concentrations in Beijing, Shenyang, Fushun, and Tieling, which are North Chinese cities, were substantially higher compared to those in Japanese (Kanazawa, Tokyo, Sapporo, and Kitakyushu) and Korean (Seoul and Busan) cities. However, the concentrations of PAHs and NPAHs were not significantly different between South Chinese cities (Shanghai and Fuzhou) and Japanese and/or Korean cities. About 95% of 2–3-ring PAHs and more than 99% of 2-ring NPAHs existed chiefly in the gas phase, while 4-ring PAHs and 3-ring NPAHs were in both the gas and particle phases, and the other PAHs and NPAHs were almost completely in the particulate phase. In each city, more than 80% of the total PAHs and total NPAHs were found in the fine particulate fraction (<2.1 μm). Cluster analyses and diagnostic ratios showed that the major contributors of PAHs and NPAHs were different in these cities because of their different energy consumption habits.

Keywords Polycyclic aromatic hydrocarbons · Nitro-polycyclic aromatic hydrocarbons · Northeast Asia · Air pollution · East Asian monsoon

9.1 Introduction

Northeast Asia is one of the most important economic regions of the world. The core countries that constitute Northeast Asia are Japan, China, Korea, and the Russian Far East. In recent years, there has been rapid economic and industrial development in these countries. The main energy sources in these countries are oil in Japan and

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Korea and coal in China/the Russian Far East. These countries account for about one third of global energy consumption with China in particular reaching 22.9% of the total global consumption in 2015 (BP 2016). The burning of these fuels and biomass releases many pollutants including polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs). Furthermore, air pollution originating from one country can be transported to other countries, making these transboundary contaminants. Therefore, the mobility of these pollutants and their risk to human health (Part VI) necessitate the monitoring of PAH/NPAHs. In this section, the atmospheric behaviors and primary contributors of PAHs/NPAHs in 13 Asian cities are reviewed.

9.2 Concentration of PAHs/NPAHs in Northeast Asia

Figure 9.1 shows the locations of the 13 sampling cities in Japan (Sapporo, Kanazawa, Tokyo, and Kitakyushu), China (Shenyang, Fushun, Tieling, Beijing, and Shanghai), Korea (Seoul and Busan), and the Russian Far East (Vladivostok). The concentrations of PAHs (left) and NPAHs (right) in these cities from 1997 to 2013 are shown in Fig. 9.2. The concentrations of the total 6 PAHs, which include pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), and benzo[*a*]pyrene (BaP), ranged from 0.7 to

Fig. 9.1 Sample city sites in Northeast Asia

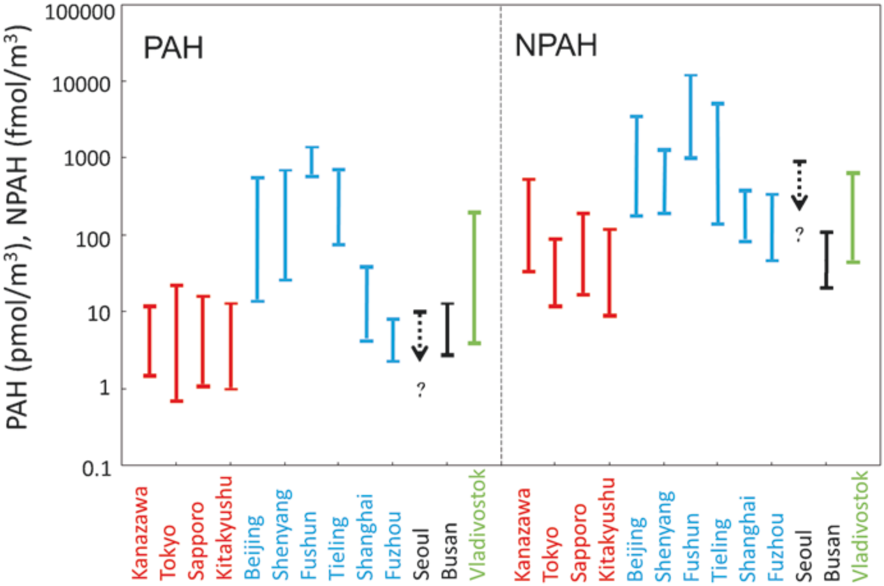

Fig. 9.2 Concentrations of atmospheric PAHs and NPAHs in 13 cities in Northeast Asia

22 pmol/m^3 of air in Japanese cities, from 2.3 to 1400 pmol/m^3 in Chinese cities, from 2.8 to 13 pmol/m^3 in Korean cities, and from 3.9 to 200 pmol/m^3 in the Russian Far East city. The concentrations of total NPAHs including 1,3-, 1,6-, and 1,8-dinitropyrenes (DNPs), 1-nitropyrene (1−NP), 6-nitrochrysene (6-NC), and 6-nitrobenzo[*a*]pyrene (6-NBaP) ranged from 9 to 530 fmol/m^3 in Japanese cities, from 47 to 12,000 fmol/m^3 in Chinese cities, from 21 to 900 fmol/m^3 in Korean cities, and from 45 to 640 fmol/m^3 in the Russian Far East city. Both PAH and NPAH levels were higher in Chinese cities and the city of the Russian Far East and lower in Japanese and Korean cities. Furthermore, PAH and NPAH levels in the cities of Northern China (Beijing, Shenyang, Fushun, and Tieling) were much higher than those in the cities of Southern China (Shanghai and Fuzhou). The concentration orders of PAHs and NPAHs were not the same in these cities, suggesting that the concentrations of PAHs and NPAHs in the atmosphere of these cities were associated with different contributors (Hattori et al. 2007; Tang et al. 2002a, b, 2005, 2009, 2013; Hayakawa 2016).

9.3 Behaviors of PAHs/NPAHs

The gas/particulate partitioning of PAHs and NPAHs in the atmosphere depends on factors such as vapor pressure, temperature, atmospheric pressure, and the concentrations and properties of dust. Vapor pressures vary widely (10^{-2}–10^{-10} mmHg,

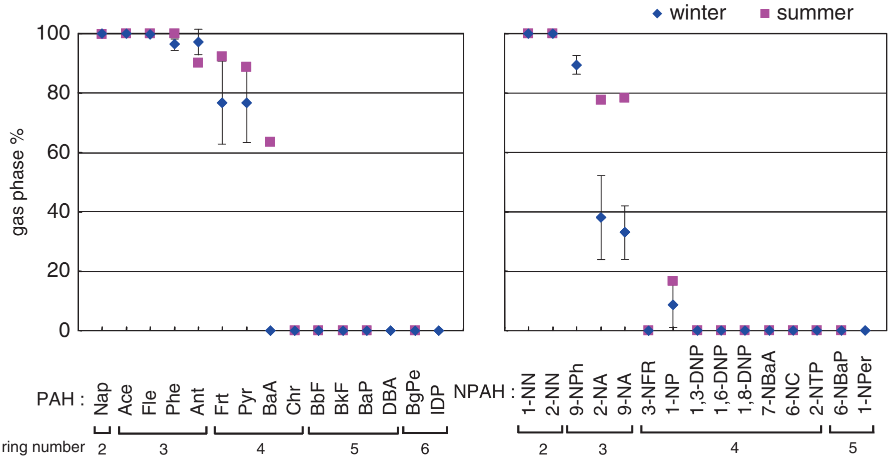

Fig. 9.3 Gas/particulate partition of atmospheric PAHs and NPAHs in Kanazawa

at 25 °C), so PAHs and NPAHs exist in both the gas and particulate phases in the atmosphere (Keller and Terry 1984; Tao et al. 2007; Yamasaki et al. 1982). Figure 9.3 shows the gas/particulate partitioning of atmospheric PAHs and NPAHs collected at an urban site in Kanazawa, Japan, during summer and winter. PAHs having two rings exist in the gas phase, and PAHs having five rings or more exist in the particle phase, while PAHs having three and four rings exist in both phases. Also, the vapor pressures of NPAHs are lower than those of the corresponding PAHs having the same ring number because of the substituent effect of the nitro group. As a result, NPAHs having four rings or more such as 1−NP exist mainly in the particulate phase, while NPAHs having two and three rings are in both phases. During summer, the ratios of PAHs having three and four rings and NPAHs having two and three rings in the gas phase were larger. The percentages of fluoranthene and Pyr, for example, increased to 16% and 11%, respectively, at 25.4 °C. Araki et al. (2009) reported that the distribution of NPAHs to the gas and particle phases in the atmosphere was also according to a Langmuir model (Araki et al. 2009).

The size of particulates in the atmosphere ranges from 50 nm to 100 μm. Coarse particulate matter (>2.5 μm, $PM_{2.5}$) is formed through natural processes such as volcanic eruptions, forest fires, and dust storms. Fine particulate matter (<2.5 μm, $PM_{2.5}$) originates from human activities, such as through vehicles and power plants. The International Agency for Research on Cancer (IARC) has categorized particulate matter in Group 1 (*carcinogenic to humans*) due to their ability to penetrate deep into the lungs (IARC 2016). In order to understand the distributions of atmospheric PAHs and NPAHs in different size particulates, airborne particulates were separately collected in some Northeast Asian cities. Figure 9.4 summarizes the particle-size distributions of total suspended particulates (TSP), PAHs, and NPAHs

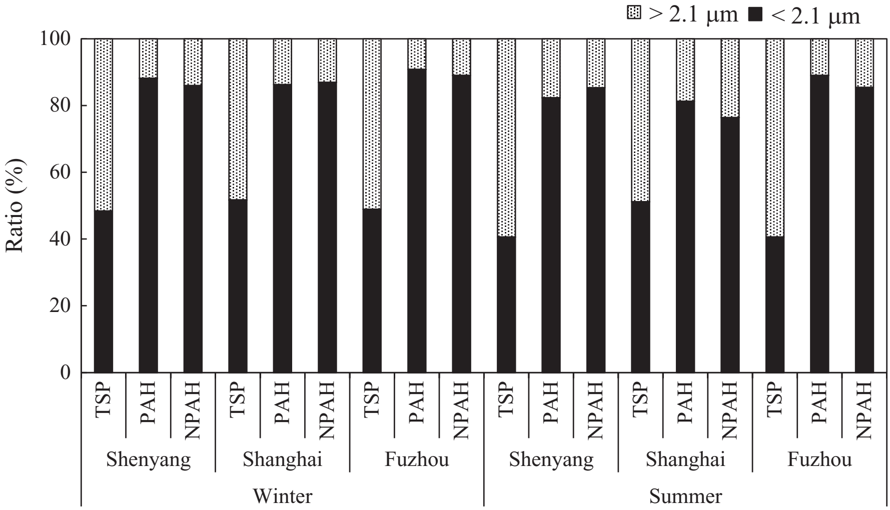

Fig. 9.4 Particulate-size distributions of TSP, PAHs, and NPAHs in Shenyang, Shanghai, and Fuzhou, China, in winter and summer

in three typical cities located between North and South China in winter and summer. For TSP, about 50% of the mass was in the finest particulate fraction (<2.1 μm), whereas more than 80% of the total PAHs and NPAHs were in this fraction in all three cities in each season (Tang et al. 2013). This result agrees with other reports studied in Japanese cities such as Kanazawa and Saitama (Hayakawa et al. 1995a; Kawanaka et al. 2004). This finest particulate fraction might be most harmful to human health, because smaller particulates go deeper into the lungs and affects their function (Lighty et al. 2000).

In the Northeast Asia region, the East Asian monsoon strongly affects the climate of these countries. A large cold, dry air mass accumulates in Northeastern Eurasia during the cold season (wind direction from west to east), and a subtropical anticyclone forms in the Northeastern Pacific Ocean and is strongest during the warm season (wind direction from east to west). Through these systems, air pollutants such as PAHs and NPAHs can be widely distributed. In our previous studies of PAHs and NPAHs at a remote Japanese background site on the Noto Peninsula (Tang et al. 2014; Yang et al. 2007) and PAHs at a suburban site in Kanazawa (Tamamura et al. 2007), atmospheric PAHs and NPAHs were strongly influenced by combustion products transported from Northeast China during winter and from Japan in summer. In areas such as in Beijing in 2009, by using back trajectory analysis and the Air Pollution Index data, it was found that high concentrations of PAHs have been influenced also by surrounding provinces, such as Hebei, Shangxi, and Liaoning (Tang et al. 2017).

9.4 Identifying the Major Contributors of PAHs/NPAHs

PAHs and NPAHs in the atmosphere originate primarily from the imperfect combustion and pyrolysis of organic matter, although some NPAHs, such as 2-NP and 2-nitrofluoranthene, are formed in the atmosphere via reactions of their parent PAHs (Arey et al. 1986; Hayakawa et al. 1995b; Rogge et al. 1993). In urban areas, PAHs and NPAHs are mainly emitted from automobiles, power plants, domestic heating sources, and industrial processes (Chen et al. 2005; Hayakawa et al. 1995b; Huang et al. 2014; Kakimoto et al. 2000, 2002; Li et al. 2015; Tang et al. 2005; Zhang et al. 2008). However, the major contributors of atmospheric PAHs and NPAHs in cities differ due to the use of different kinds of primary energies and lifestyles. Molecular diagnostic ratios and multivariate statistical analyses can be used to identify possible major contributors of atmospheric PAHs and NPAHs. Table 9.1 summarizes commonly used molecular diagnostic ratios. Since the yield of NPAHs from parent PAHs will increase with increasing combustion temperatures, ratios such as a [1−NP]/[Pyr] ratio are useful for identifying whether diesel-engine vehicles (which combust at around 2700 °C) are the major contributors or whether coal combustion (which combusts at about 900 °C) is the major contributor (Hayakawa 2016; Tang et al. 2005). [1−NP]/[Pyr] ratios were 0.003 in Shenyang (winter), 0.02 in Vladivostok (winter), 0.02 in Kitakyushu (winter), and 0.003 in Muroran. These low ratios were not very different from the ratios for coal stove particulates (Table 9.1) and other coal combustion systems such as steel industries in Kitakyushu and Muroran (Hayakawa et al. 2016; Tang et al. 2005). By contrast, this ratio reached 0.21 in Seoul (winter), 0.14 (winter) in Sapporo, 0.13 (winter) in Kanazawa, and 0.13 (winter) in Tokyo, which combined with other molecular diagnostics strongly suggests that diesel-engine exhaust particulate is a major source (Table 9.1) (Tang et al. 2005). Similarly, in other studies, the major contributors of atmospheric PAHs and NPAHs in Shanghai and Fuzhou were vehicle emissions (Liu et al. 2015; Tang et al. 2013) and in Beijing were the mixing of coal and petroleum combustion in all seasons (Feng et al. 2005; Huang et al. 2006; Jiang et al. 2009; Tang et al. 2017 Wang et al. 2009; Zhou et al. 2005).

On the other hand, multivariate analysis methods, such as principal component analysis (PCA), factor analysis (FA), and cluster analysis (CA), are often used to indicate the main sources of atmospheric PAHs and NPAHs (Hattori et al. 2007; Liu et al. 2010; Tang et al. 2005, 2009, 2011). Figure 9.5 shows an example of cluster analysis dendrogram using Ward's method and standardized squared Euclidean distance. In this case, three large clusters were observed according to the compositions of PAHs and NPAHs in three Chinese cities; cluster 1 includes Shenyang site 1 (SY-1, summer), SY-2 (summer), and SY-3 (summer). Cluster 3 includes diesel-engine vehicles (DEP) only. Other sites (Fushun sites 1–3 (FS-1–3)) and Tieling sites 1–3 (TL-1–3)/seasons (summer and winter) and coal combustion systems (CEP) were all grouped into cluster 2. The atmospheric PAHs and NPAHs in Shenyang (winter), Fushun, and Tieling seemed to be affected by coal combustion systems such as through domestic heating and factories. In Shenyang, the contribution of coal

Table 9.1 Concentration ratios of PAHs in participates from gasoline-engines, factories, diesel-engines and coal stoves

Source	[BaA]/ ([Chr] + [BaA])	[FR]/ ([Pyr] + [FR])	[BbF]/ ([BbF] + [BkF])	[BaP]/ ([BaP] + [BgPe])	[IDP]/ ([BgPe] + [IDP])	[1–NP]/ [Pyr]	References
Gasoline-engine	0.22–0.55						Simcik et al. (1999)
		0.40					Rogge et al. (1993)
			0.52–0.60				Dickhut et al. (2000)
					0.21–0.22		Khalili et al. (1995)
Factories	0.23–0.89	0.21–0.26			0.36–0.57		Yang et al. (2002)
Diesel-engine	0.38–0.64	0.60–0.70					Sicre et al. (1987)
					0.35–0.70		Rogge et al. (1993)
	0.36	0.50			0.50	0.36	Tang et al. (2005)
				0.23–0.28			Masclet et al. (1987)
Coal stove	0.50	0.53			0.33	0.001	Tang et al. (2005)
					0.35–0.69		Zhang et al. (2008)
				0.47—0.86			Daisey et al. (1979)
					0.23–0.47		Chen et al. (2005)
	0.18–0.38	0.36–0.53	0.81–0.95		0.14–0.32		Huang et al. (2014)
			0.78–0.80				Masclet et al. (1987)

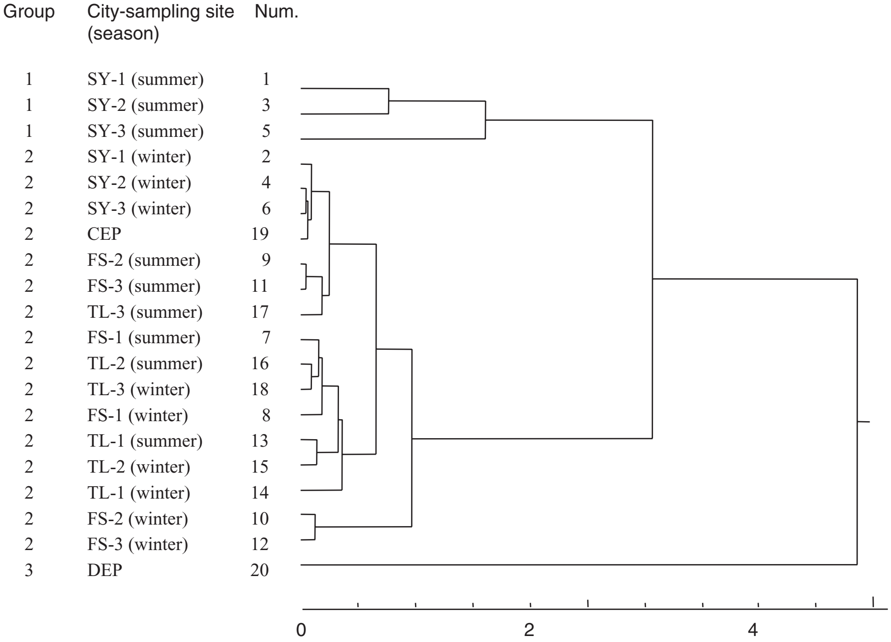

Fig. 9.5 Cluster analysis dendrogram of PAHs and NPAHs in airborne particulates collected in Shenyang, Fushun, and Tieling and in CEP and DEP by using Ward's method and standardized squared Euclidean distance

combustion systems was still observed. However, the cluster of Shenyang (summer) was far from the cluster of DEP, suggesting that the contribution of diesel-engine vehicles was not significant, even though Shenyang had the largest number of registered cars (Tang et al. 2011).

9.5 Annual Variations in PAHs/NPAH Concentrations

To reduce air pollution, national governments have advanced environmental measures. In China, the Shenyang government undertook the Blue Sky Project (*Shenyang Environmental Protection Bureau of China*), in which 100 factories were transferred to the outer city and 5000 inefficient boilers for domestic heating were removed from 2001 to 2007. These changes helped reduce the annual average concentrations of PM_{10} from 190 μg/m^3 in 2001 to 120 μg/m^3 in 2009 (SYEPB). Our previous report showed that the concentrations of PAHs decreased by 40% and 67% at SY-1 and SY-2, respectively, in winter from 2001 to 2007. However, the concentration of NPAHs did not change markedly at either site, which suggests that Shenyang's Blue Sky Project was more effective in reducing PAHs than NPAHs in winter. In summer,

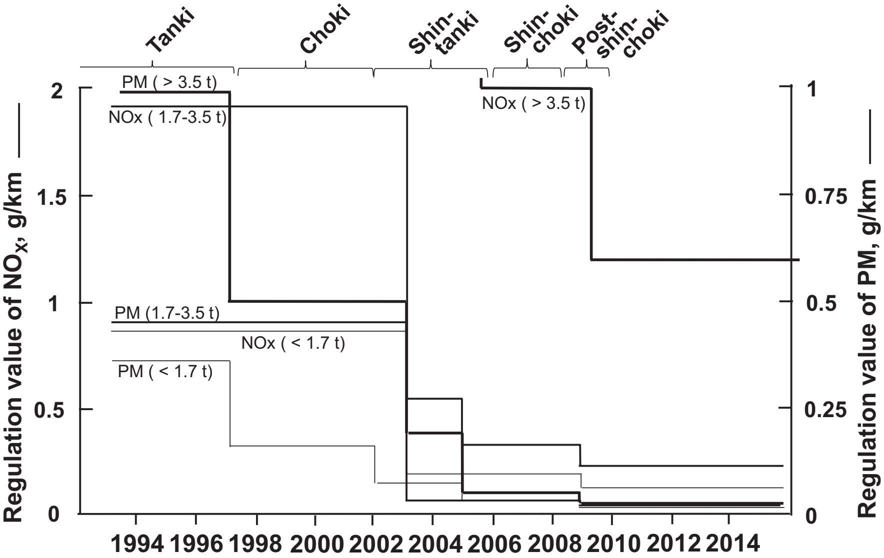

Fig. 9.6 Japanese regulation values of NO_x and PM against new diesel-engine automobiles

the concentrations of PAHs and NPAHs rose by a factor of at least 4 at both sites. A likely contributing factor was an increase in the number of motor vehicles from 360,000 in 2000 to 560,000 in 2007 (Tang et al. 2011). The Beijing government initiated environmental measures before the 2008 Summer Olympic Games that included new vehicle emission standards (European emission standards (Euro) III from 2005 and Euro IV from 2008) and restrictions on the use of vehicles. As a result, not only did PM_{10}, NO_2, and SO_2 decrease but also the concentrations of PAHs and NPAHs, by 72.6% and 93.4%, respectively, in the summers between 2004 and 2010. But in winter, NPAH levels only decreased by 53.7%. The concentration of PAHs did not significantly change. This was because the high concentrations of PAHs were influenced also by surrounding cities and provinces such as Shanxi, Hebei, and Liaoning provinces where coal combustion systems are used for domestic winter heating (Tang et al. 2017).

In Japan, from the 1970s, urban air pollution became serious with increased traffic. In the early 2000s, the Japanese government strengthened progressive countermeasures (Shin-tanki in 2003, Shin-choki in 2005, and Post shin-choki in 2009) aimed at reducing urban air pollution through emission controls of PM and NO_x from automobiles and diesel/gasoline quality control (Fig. 9.6). As a result, in Kanazawa, the concentration of PAHs decreased by 63.9% in winter and 75.6% in summer in the period between 1999 and 2010. NPAH concentrations showed significant decreases of 88.0% in winter and 89.2% in summer during the same period (Hama et al. 2012). Similar PAH/NPAH decreases were also observed in the other Japanese cities (Suzuki et al. 2015; Hayakawa 2016).

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Chapter 10
Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Thailand

Thaneeya Chetiyanukornkul, Thanyarat Chuesaard, Akira Toriba, and Kazuichi Hayakawa

Abstract Thailand has been facing increasing levels of air pollution, resulting in adverse health consequences. One of the most serious pollutants is airborne particulate matter (PM). PM contains many inorganic and organic hazardous compounds. Among them, polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are of great concern because of their severe toxicity (carcinogenicity and/or mutagenicity and/or teratogenicity) to humans. This chapter reviews ambient and indoor concentrations of PAHs and NPAHs with a focus on Chiang Mai, Thailand, and discusses their possible emission sources and health risks. In addition, concerning human intake, the concentrations of individual urinary hydroxyPAHs (OHPAHs) were measured in different Thai subjects in order to estimate their PAH exposure. Understanding PAH and NPAH distributions can be useful in order to understand their sources, sinks, and exposure risks to Thai citizens.

Keywords Polycyclic aromatic hydrocarbons · Nitropolycyclic aromatic hydrocarbons · Particulate matter, Chiang Mai, Thailand

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10.1 Introduction

Atmospheric pollution is an issue of serious environmental concern in Thailand and Southeast Asia in general. The change in land use and the emergence from an agricultural base to a more industrialized economy has Thai cities facing air pollution in many areas, resulting in adverse health consequences. The three major sources of air pollution are vehicular emissions in cities, biomass burning and transboundary haze in rural and border areas, and industrial discharge in concentrated industrialized zones (Vichitvadakan and Vajanapoom 2011). According to a World Bank estimation, the total mortalities in Thailand attributable to air pollution have risen from roughly 31,000 in 1990 to 49,000 in 2013 (World Bank 2016). Most at risk are children and the elderly, as well as people living in areas near coal-fired power plants and polluting industries. At the heart of this are the invisible and harmful pollutants; ultrafine and fine PM < 0.1 μm, < 2.5 μm, < 10 μm, in aerodynamic diameter ($PM_{0.1}$, $PM_{2.5}$, PM_{10}); and the toxic substances bound to these PM.

The criteria for PM_{10} monitoring are well documented in urban and rural areas. In cities such as Bangkok, air quality monitoring performed by the Pollution Control Department (PCD) for the past 16 years has revealed that the levels of PM_{10} have exceeded both annual (50 μg/m^3) and 24-hr. (120 μg/m^3) national standards (PCD 2017). The main source of PM_{10} in Bangkok is vehicular emissions (Chuersuwan et al. 2008). In the eastern coastal province of Rayong's industrial area, the major air pollutants are volatile organic compounds (VOCs), sulfur dioxide (SO_2), and nitrogen oxides (NO_x). Although environmental management has been instituted, levels of these air pollutants continue to exceed Thailand's standards (PCD 2016). In the rural and border areas, most notably Chiang Mai, agricultural burning and forest fires, including transboundary haze from Myanmar, have contributed to high levels of PM_{10}, which have increased to critical levels since 2006 [250 μg/m^3, 300 μg/m^3, 175 μg/m^3, 220 μg/m^3, 374 μg/m^3, 189 μg/m^3, 322 μg/m^3, 347 μg/m^3, 422 μg/m^3, 436 μg/m^3, and 371 μg/m^3 in 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, and 2016, respectively (PCD 2017)]. Moreover, the Southeast Asian haze that originate from forest fires in Indonesia have continually affected the health of residents in the southern provinces, particularly in 1996, 1997, and 2015 where the maximum PM_{10} levels reached as high as 350 μg/m^3 (PCD 2017; Chisholm et al. 2016). The representative map of cumulative hotspots in 2016 for Southeast Asia shows the differences between January–April (the dry season) and July–October (the wet season) (Fig. 10.1). For Upper Northern Thailand (eight provinces), the differences between the dry season and wet season are shown (Fig. 10.2) with the highest number of hotspots in April (Fig. 10.3). In general, the PCD of Thailand has monitored the levels of PM_{10}, while $PM_{2.5}$ is more limited. Based on 2015 data, out of 29 provinces that are equipped with air monitoring stations belonging to the PCD (Fig. 10.4), 23 exceeded the average annual PM_{10} levels. Between January and May of 2016, the five cities with the highest annual average concentrations of $PM_{2.5}$ were Chiang Mai, Khon Kaen, Lampang, Bangkok, and Ratchaburi.

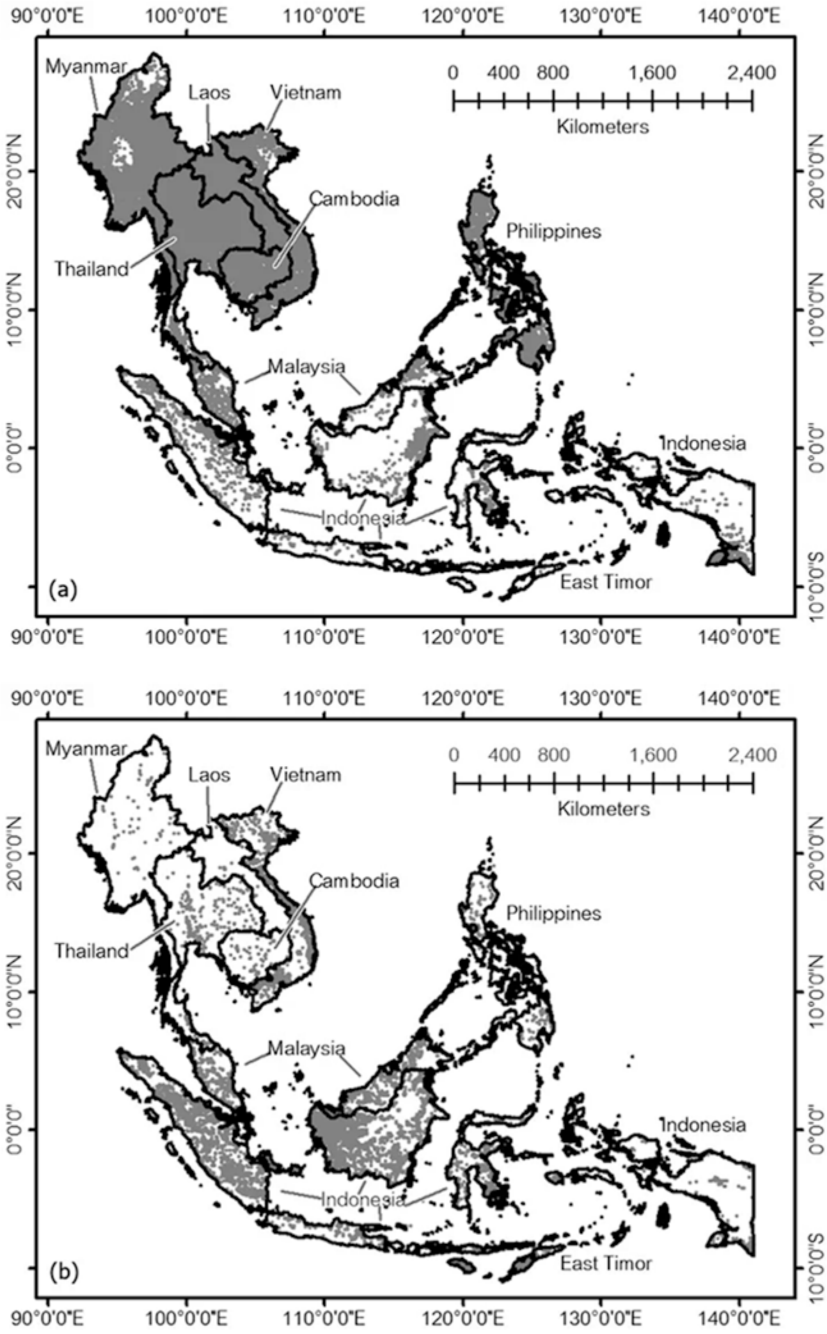

Fig. 10.1 Hotspots in Southeast Asia during January–April 2016 (**a**) and July–October 2016 (**b**)

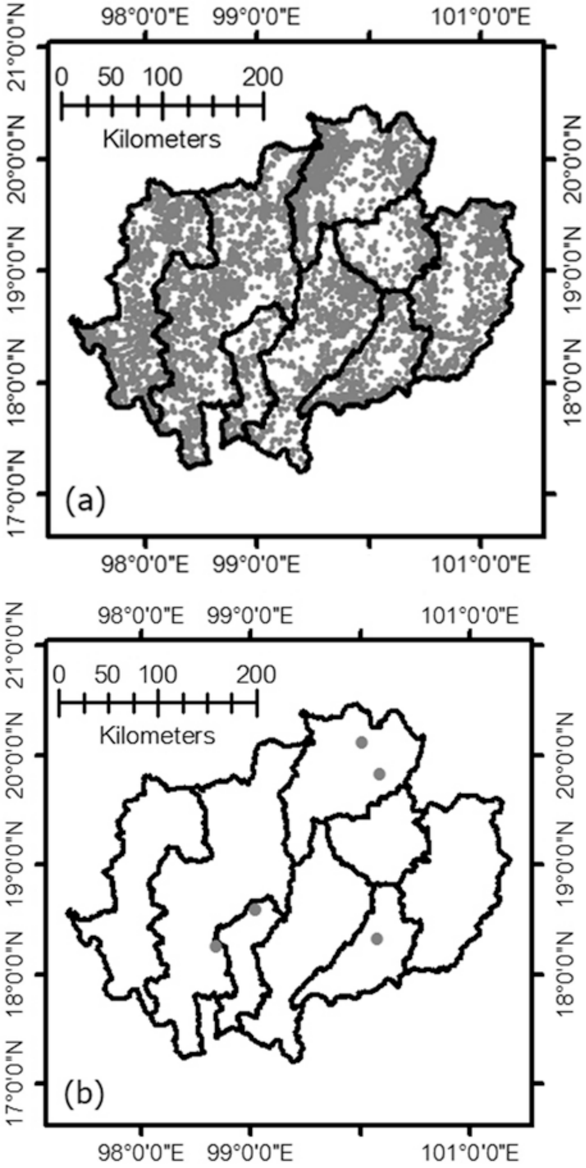

Fig. 10.2 Hotspots in eight provinces of Upper Northern Thailand during January–April 2016 (**a**) and July–October 2016 (**b**)

This means that there are levels reaching into "unhealthy," "very unhealthy," and "hazardous" levels, as categorized by the World Health Organization (WHO). Such the increasing of PM_{10} level is directly associated with the severity of chronic obstructive pulmonary disease in Chiang Rai, Upper Northern Thailand (Pramuansup et al. 2013).

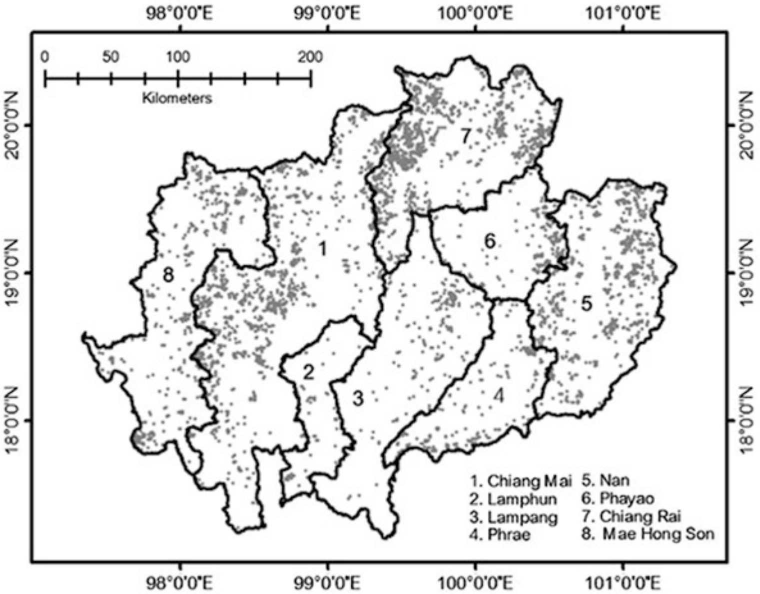

Fig. 10.3 Hotspots in eight provinces of Upper Northern Thailand in April 2016

Various toxic chemicals bound to PM need to be considered because PM penetrates the whole body, accumulating in the lungs, liver, spleen, kidney, heart, muscle, and fat (Elovaara et al. 2007). Polycyclic aromatic hydrocarbons (PAHs) and their nitro derivatives (NPAHs) are well known. They are generated through incomplete combustion and are emitted into ambient air as particles and gases. The PAH and NPAH composition differs among areas, depending on their sources and economic situations. PAHs have attracted increasing concern because of their carcinogenicity, mutagenicity, and teratogenicity (Lau et al. 2010). Although NPAHs are generally present at low concentrations in the atmosphere compared to their parent PAHs (Bamford and Baker 2003), they have been identified as direct-acting mutagens and carcinogens, which are more toxic than their parent PAHs (Durant et al. 1996). Therefore, research knowledge on PAHs and NPAHs bound to $PM_{10,2.5}$ (e.g., concentration ratios, source influences, toxicity risks, etc.) and their parent and metabolite concentrations in humans (e.g., PAHs in human hair, hydroxyPAHs in human urine, 1-nitropyrene metabolites in human urine, etc.) have become the focus of attention in recent years, both globally and within Thailand (Chetiyanukornkul et al. 2004, 2006; Hayakawa et al. 2007; Hayakawa 2016; Jariyasopit et al. 2014; Kim et al. 2013; Miller-Schulze et al. 2013; Toriba et al. 2003a, b; Toriba and Hayakawa 2007).

Chiang Mai is a popular tourist destination but faces problematic heavy smoke and $PM_{10,\,2.5}$ during the dry season. The highest daily average $PM_{2.5}$ levels from 2011 to 2016 were 75, 211, 259, 300, 373, and 207, respectively (PCD 2016). On the other hand, it was reported that from 2013 to 2016, a major cause of death for Chiang Mai residents is from cancer and tumors (Chiang Mai Provincial Public

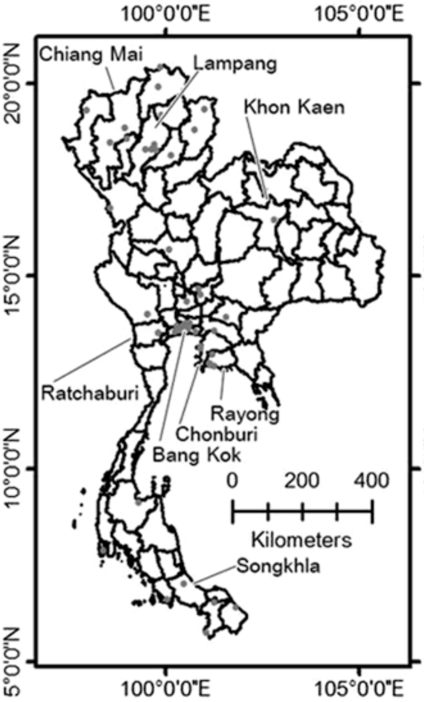

Fig. 10.4 Air monitoring stations in Thailand operated by the PCD

Health Office 2016a). Lung cancer was the most common cancer diagnosed in Chiang Mai from 2012 to 2016, while liver cancer was second (Chiang Mai Provincial Public Health Office 2016b). Thus, the main aim of this review is to provide an overview of the contemporary studies on PM-bound PAHs and NPAHs and their metabolites in humans, with a specific focus on Chiang Mai, Thailand.

10.2 Ambient Concentrations of PAHs in Thailand

Bangkok is the capital and the most populous city of Thailand. With a population of over eight million, traffic congestion and the associated air pollution are serious problems. PM_{10}-bound PAHs which were collected from six sites in Bangkok using a high-volume air sampler from 1999 to 2000. The summed PAHs based on the 20 species had an average concentration of 60 ng/m^3. Benzo[*ghi*]perylene (BghiPe), indeno[1,2,3-*cd*]pyrene (IDP), and benzo[*e*]pyrene (BeP) were the major compounds (Thongsanit et al. 2003). The characteristics of PAHs in PM_{10} from the Bangkok metropolitan area were determined, with BghiPe, benzo[*b*]fluoranthene (BbF), BeP, IDP, and benzo[*a*]pyrene (BaP) being the predominant PAHs. Correlation analysis showed that there is a close correlation between the concentration of carcinogenic PAHs and the amount of PM_{10}. This is due to the absorptivity property on the surface of particles (Norramit et al. 2005).

In 1996–1997, total suspended particulate matter in ambient air was collected using high-volume air samplers in Pathum Thani Province, 40 km north of Bangkok. The PAH profile showed relatively high concentrations of BghiPe and coronene, decreasing with distance from the road, suggesting that the main source of PAHs was vehicle emissions in Bangkok and nearby places (Kim Oanh et al. 2000).

The Southeast Asian haze, containing elevated PM_{10}, often blankets Southern Thailand during June–August. The variation in daily PM_{10} levels during this period is largely dependent on the wind directions and the intensity of fire (Pentamwa and Kim Oanh 2008). The atmospheric PAH concentration of Hat Yai City, Songkhla Province, Southern Thailand, was examined. The city is surrounded by rubber industries. Air samples were collected with a high-volume sampler at the downtown of Hat Yai City and Prince of Songkla University (PSU) in 2005. The atmospheric PAH concentrations were influenced by rubber sheet production, wind direction, and precipitation (Tekasakul et al. 2008).

The northern part of Thailand annually copes with air pollution during the dry season, but this has been particularly acute over the past 10 years. Eight affected provinces in the upper northern Thailand include Chiang Mai, Chiang Rai, Lampang, Lamphun, Mae Hong Son, Phayao, Phrae and Nan. The PM_{10} concentration increases at the beginning of the dry season (December), peaks in March, and decreases by the end of April (Pengchai et al. 2009). Chiang Mai, with a metropolitan population of nearly a million, is the largest city in northern Thailand. It is located in the Chiang Mai–Lamphun basin and is surrounded by mountains. For diurnal variation, vertical distribution and source apportionment of PAHs in Chiang Mai were investigated. The morning peaks between 6 AM and 9 AM were remarkably noticeable as a consequence of traffic emissions. Principal component analysis (PCA) highlighted the significance of biomass burnings and traffic emissions as the two dominant sources, accounting for 71.7% and 28.2%, respectively (Pongpiachan 2013). During the dry and wet seasons in 2010, PM_{10}-bound PAHs were collected in Chiang Mai. Diagnostic ratios and PCA were used to find the sources of PM_{10}-bound PAHs. It was found that the main source of air pollution in the dry season was biomass burning, whereas vehicle exhaust was the main source in the wet season (Wiriya et al. 2013). This result corresponded to a study which collected total suspended particulates (TSP) in Chiang Mai during the dry, transition, and wet seasons in 2010 (Chuesaard et al. 2014).

The characteristics of PAHs during the haze period in Lampang were investigated. Experimental results showed that the average concentration of PM_{10} during the haze period was 3.5 times higher than that during the non-burning period. The size distributions of total PAHs during the haze period were shifted toward smaller particles relative to the overall particle size distribution. The fractions of five- and six-ring PAHs bound on the particles were predominantly detected during the haze period (Phoothiwut and Junyapoon 2013). Therefore, the major sources of PM and PAHs in northern Thailand were from biomass burning and vehicle emissions. However, traffic density seems to be constant for the whole year, while biomass burning is mostly performed in the dry season, which coincides with the peak of the annual haze episode in this region (Chantara 2012; Chuesaard et al. 2014). There are many factors that contribute to the severe air pollution in the dry season. First, there is the extensive biomass burning from forest fires and agricultural burning as well as transboundary haze pollution from neighboring countries such as Laos and Myanmar. Second, the stagnant air resulting from high air pressure, calm winds, a vertical temperature inversion, and low amounts of rain is responsible for the scarce dispersion and prolonged suspension of PM containing atmospheric pollutants in the atmosphere. Finally, the topographical, basin architecture in the northern region promotes the accumulation of PM.

PAH concentrations in Southeast Asia are listed for comparison in Table 10.1. In Thailand, the mean concentration of total PAHs in the dry season in Chiang Mai (Wiriya et al. 2013) was comparable with total PAHs in the dry season in Lampang (Phoothiwut and Junyapoon 2013). However, these PAH concentrations were two times higher than those found in the roadside in Bangkok (Norramit et al. 2005). These higher concentrations may be caused by intensive biomass burning from forest fires and agricultural burning. Moreover, Bangkok is situated in a plain and near the sea, both of which promote the dispersion of air pollutants. Chiang Mai and Lampang, surrounded by mountains, are covered by a temperature inversion layer in the dry season, resulting in the accumulation of air pollutants in the lower atmosphere. Comparison with other countries in Southeast Asia shows that PAH concentrations in Chiang Mai in the dry season are ten times higher than those recorded in Malaysia (Jamhari et al. 2014). Perhaps this is due to the washout effect of the monsoon seasons in Malaysia. Moreover, the mean concentration of total PAHs in the dry season in Chiang Mai was three times higher than those found in Vietnam (Hien et al. 2007). Such different concentrations are likely due to the different sources of PAHs: biomass burning was the major source in Chiang Mai, whereas vehicle emissions were the main contributors in Ho Chi Minh City. Additionally, elevated concentrations of PAHs in Chiang Mai were also affected by several factors during the dry season as described above.

10.3 Ambient Concentrations of NPAHs in Thailand

There are only a limited number of studies observing the ambient concentrations of NPAHs in Thailand. One investigation examines 19 NPAHs in Chiang Mai (Chuesaard et al. 2014). TSP samples were collected during the dry season (February, March, and April), the transition period (May), and the wet season (August and September) in 2010. To estimate the original source of PAHs and NPAHs, levoglucosan (LG) was examined as a marker for biomass burning. It was found that the concentrations of NPAHs in the dry season were significantly higher than in the wet season, probably due to massive biomass burning, stable meteorological conditions, and the basin geomorphology of the region. Additionally, the proportion of each NPAH to the total NPAH concentrations was calculated monthly

Table 10.1 Mean concentration levels of total PAHs in Southeast Asia

Country	City	Site classification	Seasons/period	Particle size	Analysis	Total PAHs (ng/m^3)	References
Thailand	Bangkok	Roadside	Dry 2002–2003	PM_{10}	HPLC/FLD	12.59	Norramit et al. (2005)
Thailand	Chiang Mai	Suburban	Dry 2010	PM_{10}	GC/MSD	25.87	Wiriya et al. (2013)
		Suburban	Wet 2010	PM_{10}	GC/MSD	3.12	
Thailand	Lampang	Urban	Dry 2009	< 0.4 µm	GC/MS	14.7	Phoothiwut and Junyapoon (2013)
				0.4–2.1 µm	GC/MS	9.3	
				> 2.1 µm	GC/MS	5.1	
Malaysia	Kuala Lumpur, Petaling Jaya and Bangi	Urban, Semi-urban and Industrial	Monsoons 2010–2011	PM_{10}	GC/MS	2.71	Jamhari et al. (2014)
Vietnam	Ho Chi Minh	Urban (ITTE)	All	TSP	HPLC/FLD	8.7	Hien et al. (2007)
		Residential (VNU)	2005–2006	TSP	HPLC/FLD	7.6	

to show the seasonal variations in NPAH profiles (Fig. 10.5). 9-Nitroanthracene (9-NA) was the most abundant NPAH in the dry season, suggesting a strong contribution from biomass burning. The extremely high concentration and proportion of 9-NA to the other NPAHs might be caused by the low temperatures in biomass combustion and the high reactivity of PAH nitration. From this, it was proposed that 9-NA could be a marker of biomass burning and the [9-NA]/[1-NP] ratio as a suitable indicator for identifying the contribution of biomass burning. Using correlations between NPAHs and LG, as well as diagnostic ratios of [9-NA]/[1-NP] and [1-NP]/[Pyr], biomass burning was concluded to be a major source of NPAHs in the dry season, whereas vehicle exhaust was the main contributor in the wet season (Chuesaard et al. 2014).

Carcinogenic risk was estimated using toxic equivalent factors (TEFs) as described by Albinet et al. (2008). Carcinogenic risk was calculated using eight PAHs and five NPAHs. The relationship between monthly concentrations of PAHs, NPAHs, and total carcinogenic risk is shown in Fig. 10.6. The high concentrations of PAHs and NPAH were consistent with high carcinogenic risk. The carcinogenic risk in February were 6.2 times higher than the average risk in the wet season, indicating more harmful air conditions in the dry season than in the wet season. The risks are comparable with those observed in Maurienne, France (Albinet et al. 2008), which is a heavy-duty international traffic area. Although the atmospheric concentrations of NPAHs were lower than those of PAHs and the risks were calculated using only 5 NPAHs, the risk from NPAHs is 21% of the total risk in August. Therefore, the determination of NPAHs levels in ambient air is important for assessing health risks.

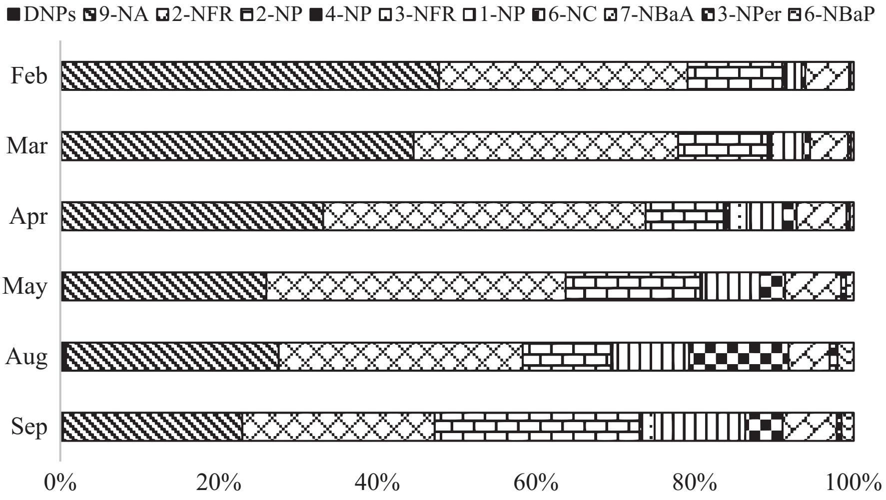

Fig. 10.5 Monthly composition profiles of NPAHs

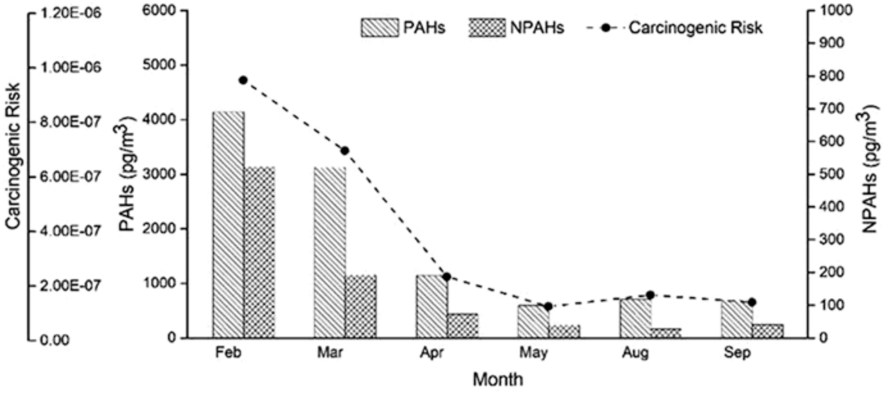

Fig. 10.6 Correlation between monthly concentrations of PAHs, NPAH, and total carcinogenic risk

10.4 Indoor Concentrations of PAHs and NPAHs in Thailand

Biomass fuel combustion for cooking is a major source of hazardous pollutants which impacts indoor air quality and human health. Two rural households in Chiang Mai, which used biomass fuels for cooking, were investigated (Orakij et al. 2017). House 1 was built of concrete blocks with a galvanized iron roof and had no windows. There were 17 people in the family and used 2 traditional open wood stoves. House 2 was a wooden structure and had better ventilation than house 1. There were two people in the family and used an open fire. $PM_{2.5}$ samples were collected both inside and outside the houses during cooking and noncooking periods. Real-time monitoring of indoor $PM_{2.5}$ during the sampling periods is shown in Fig. 10.7. $PM_{2.5}$ concentrations in the cooking periods (dinner and breakfast) were higher than the mean counts in the noncooking periods. Indoor and outdoor concentrations of total PAHs, NPAHs, and LG during cooking and noncooking periods are shown in Fig. 10.8. The indoor concentrations during cooking period were higher than noncooking periods. The concentrations during cooking in house 1 were significantly higher than those in house 2, due to a greater consumption of fuels as a result of the greater number of residents. The highest concentrations of PAHs and NPAHs were observed inside the house during cooking with mean concentrations of 9980 ng/m^3 and 18,700 pg/m^3, respectively. Benz[*a*]anthracene (BaA), benzo[*k*]fluoranthrene (BkF), and BaP were the predominant PAHs, while 9-NA was the predominant NPAH. The correlation coefficient ($p < 0.01$) of PAHs and NPAHs, using LG as a marker, confirmed that the major source of PAHs and NPAHs was biomass burning.

Carcinogenic risk was calculated and is shown in Fig. 10.9. The total risk of indoor exposure during cooking periods was much higher than in non-cooking periods or at outdoor sites. Carcinogenic risk due to indoor air contamination during cooking in house 1 was higher in house 2 because of the differences in house struc-

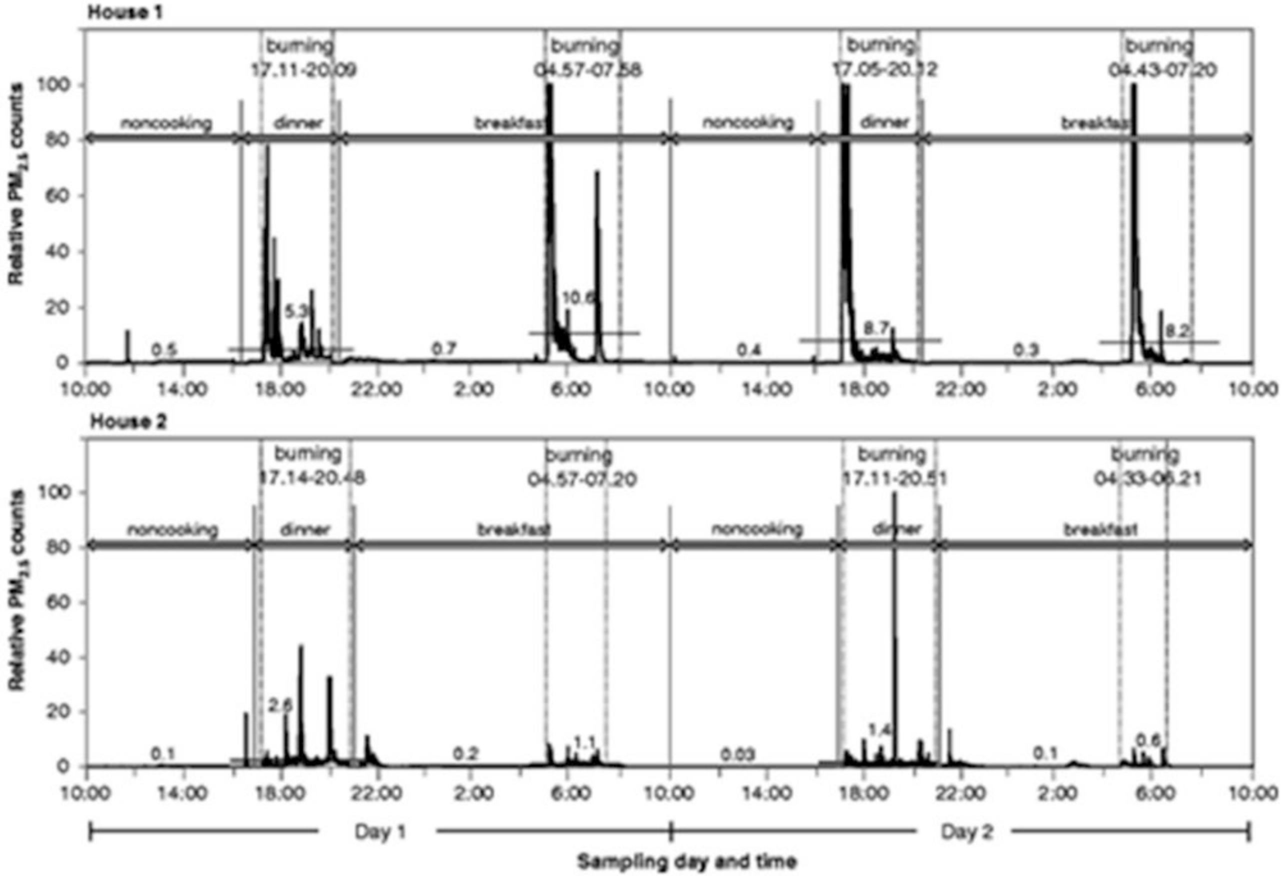

Fig. 10.7 Time-dependent changes in indoor $PM_{2.5}$ counts. The highest level of $PM_{2.5}$ was taken as 100. The details of the three sampling periods (noncooking, dinner, and breakfast) were described in the section on the "Study site and PM sampling." Horizontal lines and the values in the figure show mean values of $PM_{2.5}$ counts during burning and non-burning periods

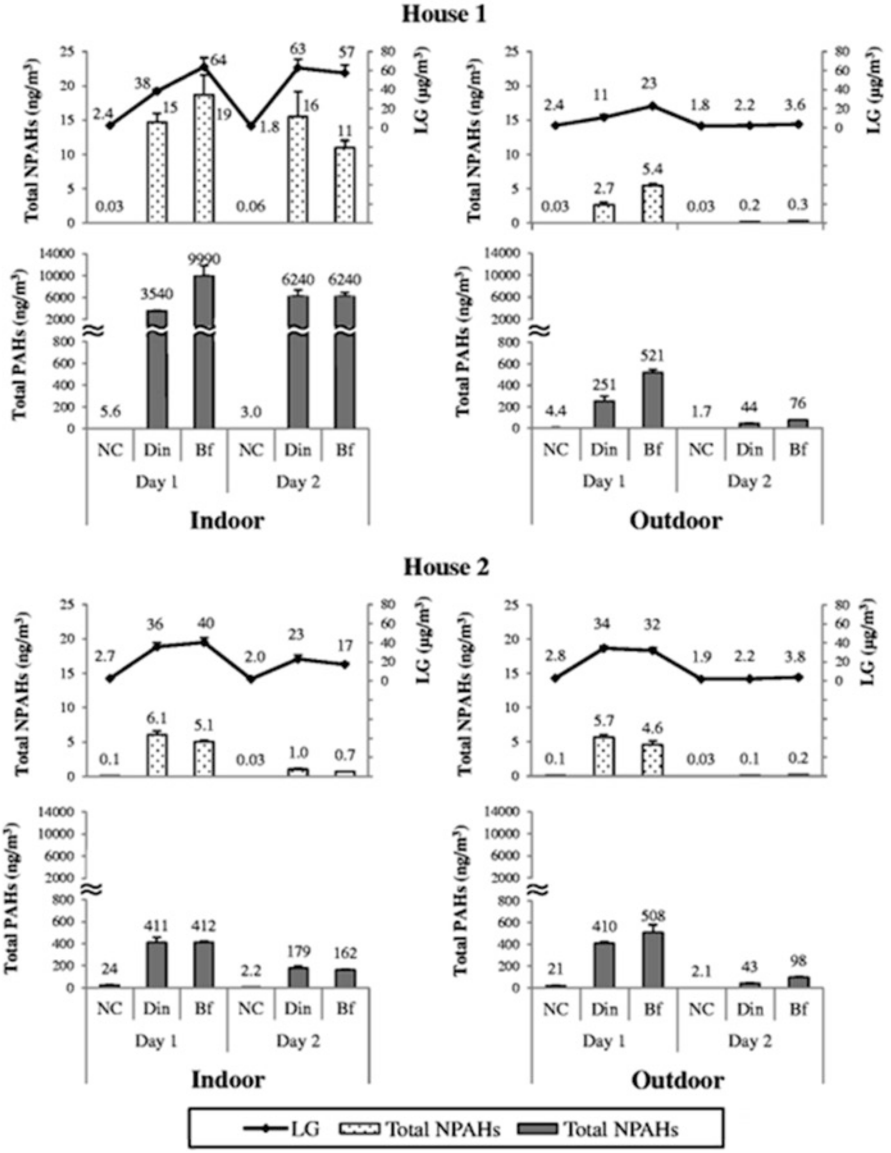

Fig. 10.8 Indoor and outdoor concentrations (mean ± SD) of total PAHs (ng/m^3), NPAHs (ng/m^3), and LG (μg/m^3) during cooking (dinner and breakfast) and non-cooking periods. NC, non-cooking; Din, dinner; Bf, breakfast

ture and fuel consumption. During cooking periods, carcinogenic risk exceeded the WHO guideline values and would be classified as a “definite risk.” This suggests that inhalation exposure due to biomass burning emissions in houses may increase the risk of lung cancer in this area.

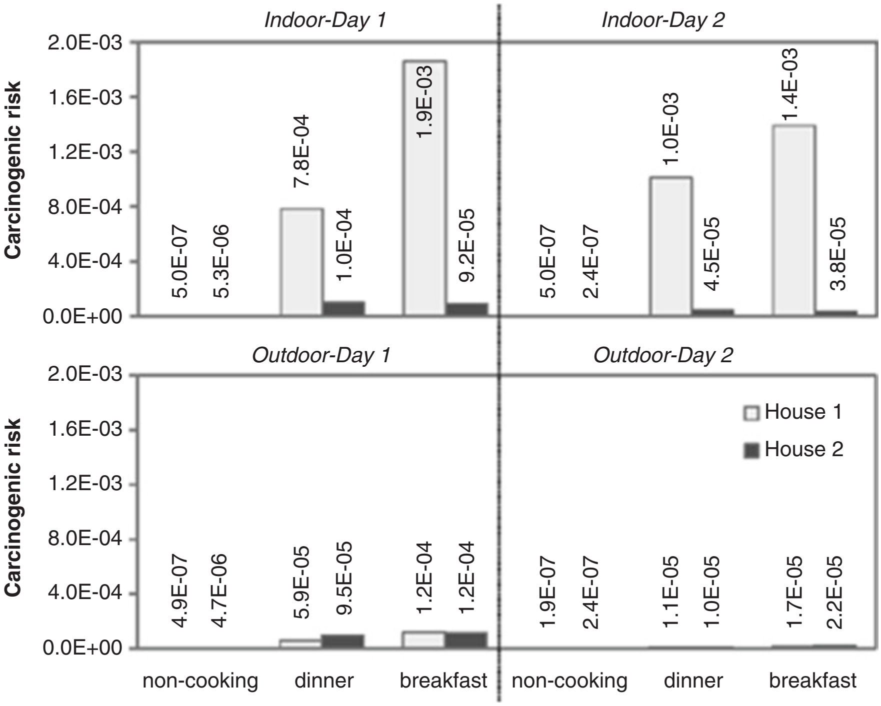

Fig. 10.9 Carcinogenic risk calculated indoors and outdoors at houses 1 and 2 during cooking (dinner and breakfast) and non-cooking periods

10.5 Human Exposure to PAHs and NPAHs (Metabolites in Urine)

Since humans are usually exposed to complex mixtures of PAHs and NPAHs, suitable metabolites in biological samples have been investigated as potential biomarkers of exposure (Chetiyanukornkul et al. 2004, 2006; Toriba et al. 2007; Toriba and Hayakawa 2007). Urinary metabolites are used because of the noninvasiveness and convenience in their analyses (Toriba et al. 2007). The evidence of negative health effects of PAH and NPAH contamination in ambient and indoor air in Chiang Mai, Thailand (Chuesaard et al. 2014; Orakij et al. 2017), can be associated with much higher incidence of lung cancer in Chiang Mai compared to other cities in Thailand (Vatanasapt et al. 1995; Wiwatanadate 2011). Therefore, PAH exposure levels to Thai subjects, especially Chiang Mai residents, have been investigated. Only published data on PAH metabolites in Thai subjects are reported. Using urinary markers, predominantly 1-hydroxypyrene (1-OHPyr), human PAH exposure has been investigated (Ruchirawat et al. 2005, 2007; Petchpoung et al. 2011; Naksen et al. 2017). Interestingly, it was found that rural school children in Chiang Mai had about four to five times and nine times higher urinary 1-OHPyr levels than urban school children in Bangkok and Chonburi, respectively (Naksen et al. 2017; Ruchirawat et al. 2007). It should be noted that pyrene and/or some PAHs in Chiang Mai's ambient air are higher than Bangkok's and Chonburi's ambient air. Non-smoking adult villagers living in Chiang Mai's rural area had ten times higher urinary 1-OHPyr levels than adult bus drivers in Bangkok (Chetiyanukornkul et al. 2006; Petchpoung et al. 2011). Urinary 2-hydroxyfluorene (2-OHFle), a major metabolite of fluorene and a known endocrine disruptor, was first observed as a more suitable biomarker than 1-OHPyr for PAH exposure from smoking (Toriba et al. 2003a). Significant differences in 2-OHFle were clearly observed between smokers and nonsmokers of both Japanese (living in Kanazawa City) and Thai (living in Chiang Mai City) subjects who otherwise had little occupational exposure to PAHs (Chetiyanukornkul et al. 2004). Unexpectedly, the urinary concentrations of both 2-OHFle and 1-OHPyr of Thai smokers were higher than those of Japanese smokers, and the urinary 1-OHPyr concentrations of Thai nonsmokers were higher than Japanese smokers, indicating that the background PAH concentrations seem to be relatively high in Chiang Mai City. Our previous studies pointed out that considering multiple biomarkers of OHPAHs would provide more comprehensive results to estimate individual exposure to PAHs. The simultaneous determination of eight urinary OHPAHs, hydroxylated metabolites of naphthalene (1-OHNap and 2-OHNap), fluorene (2-OHFle), phenanthrene (2-OHPhe, 3-OHPhe, 1–9-OHPhe and 4-OHPhe), fluoranthene (3-OHFrt), and pyrene (1-OHPyr) was developed and applied to measure their concentrations in Chiang Mai residents who were rural villagers, taxi drivers, and traffic policemen (Chetiyanukornkul et al. 2006). Table 10.2 summarizes the concentrations of OHPAHs, which are related to PAH exposure. The highest urinary levels of several OHPAHs from rural villagers were likely due to atmospheric PAHs produced by open burning for agricultural purposes in the outdoors and by biomass burning (wood and charcoal) for cooking and heating indoors. Together, indoor air quality of PAHs should be monitored to understand human exposure to PAHs. Thus, the monitoring of PAH intake using a personal air sampler, coupled with the analysis of PAH metabolites in human urine, can help determine PAH exposure via inhalation. Further research based on the urinary metabolites of PAH derivatives, including NPAHs, in Chiang Mai residents is of interest, both in order to determine the concentration levels of NPAHs and their metabolites and also to identify their more hazardous effects on humans. The routine analysis of some PAH metabolites may also be necessary to estimate the degree of PAH exposure.

10.6 Summary

Air pollution in Thailand has been rapidly increasing as a result of population growth and economic development. Vehicle emissions were the main source of air pollution in urban areas. Biomass burning was the main source in upper northern Thailand during the dry season and affected the southern region during the wet season. The variation in PM, PAH, and NPAH levels in the atmosphere was dependent

Table 10.2 Investigated urinary OHPAHs levels in mainly Thai associated with different subjects

Reference/comment	Thailand/Japan		n	Age	Concentration (μ mol/mol creatine)	
Chetiyanukornkul et al. (2004)	Chiang Mai	Non-smoking adults	3	26–47	2-OHFle = 0.22	1-OHPyr = 0.05
(non-occupational exposure to PAHs, during 2002)		Smoking adults	5	32–76	2-OHFle = 0.75[c]	1-OHPyr = 3.03[a]
[a]Significantly different from non-smoker ($p < 0.05$)	Kanazawa	Non-smoking adults	4	22–51	2-OHFle = 0.04	1-OHPyr = 0.01
[b]Significantly different from non-smoker ($p < 0.01$)		Smoking adults	10	23–69	2-OHFle = 0.26[b]	1-OHPyr = 0.12
[c]Significantly different from non-smoker ($p < 0.001$)						
Ruchirawat et al. (2005)	Bangkok	Clothes vendors	11	18–40	1-OHPyr morning = 0.04	1-OHPyr afternoon = 0.11[a,b]
(occupational and non-occupational exposure to PAHs, during 2002)		Grilled-meat vendors	14		1-OHPyr morning = 0.10	1-OHPyr afternoon = 0.10[a]
		Monks and nuns	11		1-OHPyr morning = 0.02	1-OHPyr afternoon = 0.03
[a]Significantly different from monks/nun ($p < 0.001$)						
[b]Significantly different from morning ($p < 0.005$)						
Chetiyanukornkul et al. (2006)	Chiang Mai	Rural villagers	10	25–62	1-OHNap = 7.58	2-OHNap = 12.14[b]
(study subject exposed to PAHs, during 2002)					2-OHFle = 2.62[b]	2-OHPhe = 0.82[b]
[a]Not detected					3-OHPhe = 1.15[b]	1-and 9-OHPhe = 0.51[b]
[b]Significantly different from taxi driver and traffic policeman ($p < 0.001$)					4-OHPhe = 0.09[c]	3-OHFrt = nd[a]
					1-OHPyr = 1.2 [b]	
[c]Significantly different from taxi driver and traffic policeman ($p < 0.05$)		Taxi drivers	10		1-OHNap = 6.61	2-OHNap = 2.28
					2-OHFle = 0.34	2-OHPhe = 0.15
					3-OHPhe = 0.19	1-and 9-OHPhe = 0.1
					4-OHPhe = 0.02	3-OHFrt = nd
					1-OHPyr = 0.27	

		Traffic policemen	10		1-OHNap = 4.67	2-OHNap = 2.74
					2-OHFle = 0.37	2-OHPhe = 0.11
					3-OHPhe = 0.11	1-and 9-OHPhe = 0.13
					4-OHPhe = 0.03	3-OHFrt = nd
					1-OHPyr = 0.18	
Ruchirawat et al. (2007)	Bangkok	School children	106	10–12	1-OHPyr morning = 0.18[a]	1-OHPyr afternoon = 0.20[a]
(non-occupational exposure to PAHs, during 2002)	Chonburi	School children	61		1-OHPyr morning = 0.10	1-OHPyr afternoon = 0.09
[a]Significantly different from Chonburi ($p < 0.001$)						
Petchpoung et al. (2011)	Bangkok	Adult bus drivers	100	33–53	1-OHPyr all control = 0.032	1-OHPyrAll exposed = 0.124[a]
(occupational exposure to PAHs)		Non-smokers	26		Control-non-smoker = 0.025	Exposed-non-smokers = 0.108[a]
[a]Significantly different from control ($p < 0.001$)		Smokers	74		Control-smoker = 0.045	Exposed-smokers = 0.130[a]
	Rural areas	Control group	100			
		Non-smokers	66			
		Smokers	34			
Naksen et al. (2017)	Chiang Mai	School children	202	9–12	1-OHPyr All = 0.51	
(non-occupational exposure to PAHs, during smoke haze episode in 2015)					Exposed cigarette smoke = 0.64	Non-exposed = 0.54

on sources, meteorological conditions, and geographical characteristics in each area. Airborne particulate matter consists of PAHs and NPAHs which can adversely affect human health. Biomonitoring of the exposure to PAHs in Chiang Mai subjects and other subjects is an effective strategy for monitoring exposure. Management issues related to fuel combustion, biomass and non-biomass burning, and the Thai lifestyle should be addressed, based on the available research. Further monitoring of ambient and indoor PAHs, NPAHs, and human exposure in crisis areas is also necessary for assessing health risks in Thailand.

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Chapter 11
Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Motorcycle Exhaust

Chau Thuy Pham

Abstract This study investigated the polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) in airborne particulates, soil, and motorcycle exhaust in Hanoi city. This was performed in order to understand the environmental behaviors of PAHs and NPAHs and the contribution of motorcycles to soil and atmospheric PAHs and NPAHs in a typical motorcycle city of Vietnam. The atmospheric PAHs and NPAHs distribution in Hanoi were characterized and showed a higher contribution of six-ring PAHs: benzo[*ghi*]perylene (B*ghi*Pe), indeno[1,2,3-*cd*]pyrene (IDP) and the four-ring NPAH: 7-nitrobenz[*a*]anthracene (7-NB*a*A) in a motorcycle city compared to those in typical automobile cities (Kanazawa and Tokyo, Japan) and a coal-burning city (Shenyang, China). This study showed that the concentration of benzo[*a*]pyrene (BaP), the most toxic PAH, was exhausted from motorcycles at much higher concentrations than from automobiles. Furthermore, among four detected NPAHs, 6-nitrochrysene (6-NC) and 7-NBaA were the dominant compounds in motorcycle exhaust. These may contribute to their higher concentrations in the atmosphere and soil in Hanoi. This study also found that despite small engine sizes, motorcycles emitted much more particulate matter (PM) and PAHs than automobiles. PM emitted from motorcycles showed stronger PAH-related carcinogenicity and indirect-acting mutagenicity but weaker NPAHs-related direct-acting mutagenicity than PM from automobiles. This study provides useful information to control environmental pollution and to improve air quality in motorcycle cities in Southeast Asia.

Keywords Polycyclic aromatic hydrocarbons · Nitropolycyclic aromatic hydrocarbons · Motorcycle exhaust · Airborne particulates · Soil

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11.1 Introduction

Air pollution is an important public health problem in most cities of Southeast Asian countries, including Vietnam. Hanoi, the capital and the second largest city in Vietnam, has a warm humid subtropical climate that is typical of Northern Vietnam. In recent decades, Hanoi has faced serious air pollution issues. According to air quality index (AQI) data measured by the US Embassy in Hanoi, the AQI has reached alarming levels (U.S. Embassy Hanoi 2016). Developed by the US Environmental Protection Agency, the AQI is an index for reporting daily air quality and is calculated for five major air pollutants regulated by the Clean Air Act: ground-level ozone, particulate matter, carbon monoxide, sulfur dioxide, and nitrogen dioxide. The AQI was considered as a yardstick that ranges from 0 to 500. The higher AQI value, the greater the air pollution and the greater the health concern. As reported in the National State of Environment Report on air quality (MONRE 2014), the air quality conditions were unhealthy (AQI =101–200) in 40–60% of the monitored days in Hanoi, between 2010 and 2013. Over several days, the air quality conditions were at very unhealthy (AQI = 201–300) or hazardous (AQI > 300) levels. The declining air quality in Hanoi has been attributed to the large number of vehicles running on limited road infrastructure, construction of roads and houses/buildings, and other industrial and domestic activities around Hanoi (MONRE 2014).

High-density traffic is a major reason for the air pollution problem in Hanoi city and needs to be properly managed to reduce adverse effects. The recent growth in the number of vehicles and the poor road infrastructure cause frequent traffic jams, especially during the rush hours on weekdays, and have worsened the air pollution problem. Motorcycles comprise the largest share (> 90%) of the road transport vehicles in Hanoi city, and their numbers in the city have increased at a rate of 16% per year between 2000 and 2008, with a total of over 2 million vehicles in 2008 (Kim Oanh et al. 2012). By September 2011 this number was at 3.9 million and is expected to rise to 11 million by 2025 (Tran et al. 2012). The city government has proposed a ban on motorcycles, but the proposal has been met with strong public opposition since motorcycles are still the cheapest and most convenient mode of transportation in Vietnam.

Motorcycles are well known as a major contributor to air pollution and potential sources of mutagens and carcinogens such as polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) in urban areas (Leong et al. 2001; Hien et al. 2007; Kim Oanh et al. 2012). Exhaust emitted from motorcycles contributes significantly to concentrations of atmospheric fine particulates with a diameter smaller than 2.5 µm ($PM_{2.5}$) (Kleeman et al. 2000; Yang et al. 2005). Most carcinogenic PAHs and NPAHs have been found to associate with particulates, predominantly with fine particulates (Westerholm et al. 1991; Yang et al. 2005). Ly et al. (2016) showed that the level of airborne particles measured in Hanoi were positively associated with daily hospital admissions for respiratory disease among children <5 years old. Hanoi residents have also recorded higher rates of respiratory diseases than residents in Ho Chi Minh city, according to a 2013 National

Environment Report (MONRE 2013). Although many studies have examined PAH and NPAH emissions in Asian countries such as China, Japan, Russia, and Thailand (Chetwittayachan et al. 2002; Bi et al. 2003; Chang et al. 2006; Hayakawa et al. 2007) and from automobile exhausts (Kleeman et al. 2000; Robert et al. 2007; Riddle et al. 2007), little is known about the occurrence of PAHs and NPAHs from motorcycle exhaust and how atmospheric PAH and NPAH distributions in a typical motorcycle city differ from those in automobile cities. Thus, an integrated case study was conducted to report on the occurrence of PAHs, NPAHs in Hanoi, as a typical motorcycle city with the following purposes: (1) to characterize PAHs and NPAHs in the atmospheric environment of a typical motorcycle city by comparison between automobile and coal-burning cities, (2) to investigate the contribution of PAHs and NPAHs exhausted from motorcycles to the Hanoi atmosphere, and (3) to explore the relationship between atmospheric and soil PAH/NPAH concentrations.

11.2 Characterization of Atmospheric PAH and NPAH Emissions in Hanoi

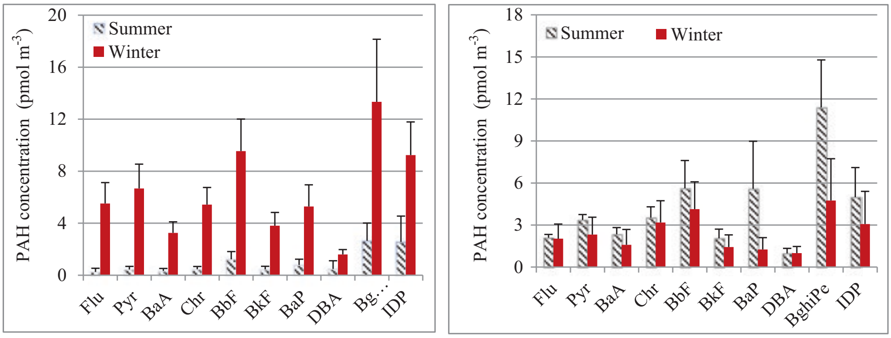
To understand the composition and distribution of PAHs and NPAHs in the atmosphere of Hanoi city, airborne particulates were collected at two representative sites using a 120H high-volume air sampler (Kimoto Electric Company Limited, Osaka, Japan) at a flow rate of 1000 L min^{-1} (Pham et al. 2012). The location of sampling sites is shown in Fig. 11.1. The first sampling site is located in a mixed residential, commercial, and institutional area (site I). This site is next to the only old inner-city industrial zone remaining in the center of Hanoi city. The second sampling site is located in one of the heaviest traffic areas of Hanoi (site T). The sampling time was conducted over a continuous period of 24 h for seven consecutive days in the summer (August, 2010) and winter (February, 2011). The total suspended particulate matter (TSP) samples were collected on Pallflex 2500QAT-UP membrane filters. Both PAHs and NPAHs on filter papers were twice extracted through ultrasonication with benzene/ethanol. Fifteen PAHs were determined by using an HPLC with a fluorescence detector, and 11 primary formed NPAHs were determined using an HPLC with a chemiluminescence detector and a column switch according to the procedure described in our previous studies (Liu et al. 2007).

The mean and standard deviations of PAH and NPAH concentrations at two sites in two seasons are shown in Fig. 11.2. The findings show that the predominant PAHs at both sites in both seasons were six-ring PAHs, benzo[*ghi*]perylene (B*ghi*Pe) and indeno[1,2,3-*cd*]pyrene (IDP), and five-ring PAHs, benzo[*b*]fluoranthene (B*b*F) and benzo[*a*]pyrene (B*a*P). The greater the molecular weight of the PAHs, the greater the toxicity. The most abundant NPAHs found in atmospheric particulates of Hanoi city were 9-nitroanthracene (9-NA), 1-nitropyrene (1-NP), and 7-nitrobenz[*a*]anthracene (7NB*a*A). These compounds are primary NPAHs found in diesel engine exhaust (Scheepers et al. 1995; Perrini et al. 2005). In general, the total concentration

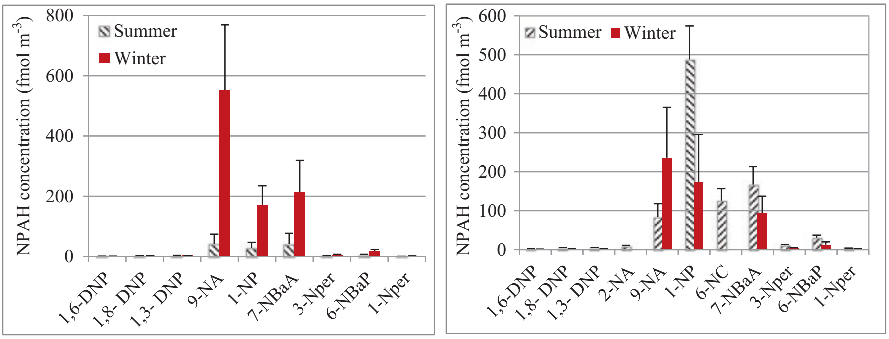
Fig. 11.1 Sampling sites in the Vietnam capital, Hanoi

of 10 PAHs and 11 NPAHs at site T, which is a heavy traffic site, was much higher than the concentration at site I, which is a mixed site in the summer but only about half the concentration at site I in the winter. Seasonal variation in PAH and NPAH levels was also examined in this study. The concentrations of individual PAHs and NPAHs were higher in the winter at site I but lower in the winter at site T. However, we observed clear differences in the ratio of four-ring/six-ring PAHs ([Flu] + [Pyr] + [B*a*A] + [Chr]/[B*ghi*Pe] + [IDP]) between the summer and winter with lower ratios in the summer than in the winter at both sites. This may be due to higher temperatures and stronger sunlight in the summer increasing the degradation of lower molecular weight PAHs.

The concentrations and distributions of PAHs and NPAHs in atmospheric particulates of Hanoi, a typical motorcycle city, were compared to those in other Asian cities including typical automobile cities in Japan (Tokyo and Kanazawa) and a typical coal-burning city in China (Shenyang) (Tang et al. 2005; Hayakawa et al. 2007), to show the composition of PAHs and NPAHs in a typical motorcycle city. This study found that the total mean concentration of nine PAHs were about 3.5



Site I Site T



Site I Site T

Fig. 11.2 PAH and NPAH concentrations in Hanoi city
Boxes and bars show the averages and standard deviations

times higher than the values at Kanazawa and Tokyo but only 6% of the value at Shenyang (Fig. 11.3). And the total average concentration of 5-NPAHs (9-NA, 1-NP, 7-NBaA, 6-NBaP, and 1-Nper) was three and six times higher than the values in Tokyo and Kanazawa, respectively, but only 16% of the value in Shenyang (Fig. 11.4). The proportion (%) of six-ring PAHs at both sites in Hanoi was considerably higher than that in automobile cities and also much higher than in a coal-burning city. The differences in six-ring PAH proportions between Hanoi and other cities were about 8–28% in summer and 10–28% in winter (Fig. 11.5). These results may be the results of the large volume of motorcycles without catalytic converters in Hanoi, where motorcycles account for around 90% of the total transportation (Pham et al. 2012). Furthermore, the poor maintenance of most light-duty and heavy-duty vehicles might be a possible reason for the composition differences. Motorcycles without catalytic converters and light-duty gasoline engines may emit large amounts of six-ring PAHs rather than four-ring and five-ring PAHs. This result is in agreement with previous reports that large PAHs such as B*ghi*Pe and coronene (Cor) are the most abundant PAHs emitted from non-catalyzed engines and light-duty gasoline engines (Rogge et al. 1993; Caricchia et al. 1999; Riddle et al. 2007).

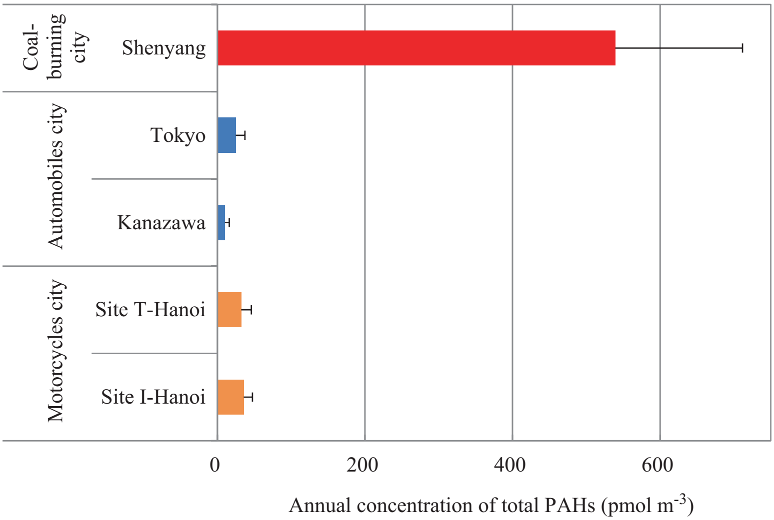


Fig. 11.3 Annual concentrations of total PAHs in Hanoi and other cities
Total PAHs = [Flu] + [Pyr] + [BaA] + [Chr] + [BbF] + [BkF] + [BaP] + [BghiPe] + [IDP]; error bars show standard deviations of the average. Data from studies of Kanazawa, Tokyo, and Shenyang are cited from our previous reports (Tang et al. 2005; Hayakawa et al. 2007) and are used for the calculation

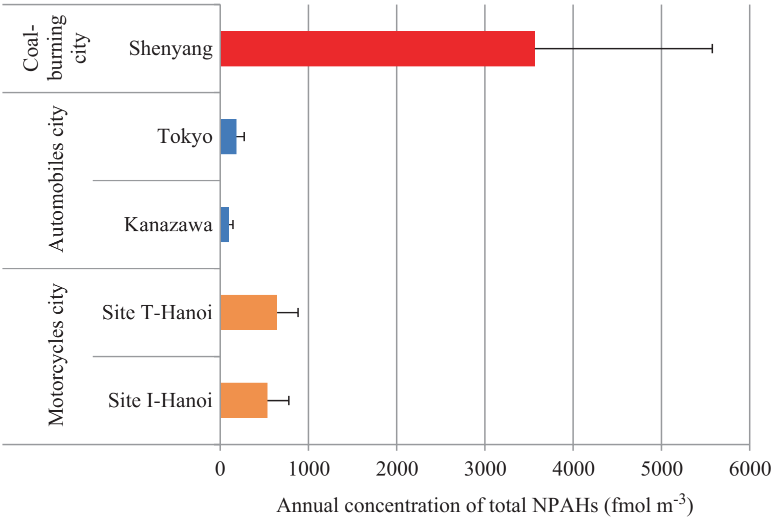


Fig. 11.4 Annual concentrations of total NPAHs in Hanoi and other cities
Total NPAHs = [9-NA] + [1-NP] + [7-NBaA] + [6-NBaP] + [1-NPer]; error bars show standard deviations of the average. Data from Kanazawa, Tokyo, and Shenyang studies cited from our previous reports (Tang et al. 2005; Hayakawa et al. 2007) are used for the calculation

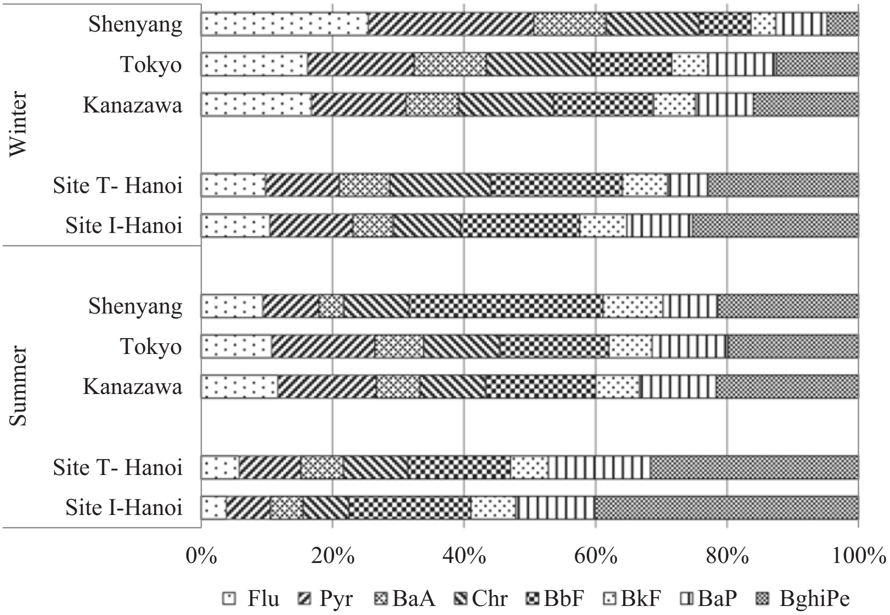


Fig. 11.5 Comparison of atmospheric PAH distributions between Hanoi and other cities
Four-ring PAHs = [Flu] + [Pyr] + [BaA] + [Chr]; five-ring PAHs = [BbF] + [BkF] + [BaP]; six-ring PAHs = [BghiPe] + [IDP]. Data from Kanazawa, Tokyo, and Shenyang studies cited from our previous reports (Tang et al. 2005; Hayakawa et al. 2007) were used for the calculation

11.3 Emission Sources of PAHs and NPAHs in Hanoi City

This study used molecular diagnostic ratios to identify emission sources of PAHs and NPAHs in the atmosphere. The [NPAH]/[PAH] concentration ratios of three pairs, [1-NP]/[Pyr], [6-NBaP]/[BaP], [7-NBaA]/[BaA], were selected as they could help identify the source contributors. As NPAH formation depends on combustion temperature, increasing significantly with rising temperature, the composition of NPAHs also changes, and inferences can be made based on these types of ratios (Tang et al. 2005). Among examined NPAHs, 1-NP has been recognized as a primary formed NPAH from automobile exhaust and an indicator for diesel engine emissions. In this report, the average [1-NP]/[Pyr] ratio (in particulate phase) was relatively higher at site T (0.11) than at site I (0.045). The value at site T was closer to the ratio for diesel engines (0.36). Furthermore, the lowest ratio of [1-NP]/[Pyr] (0.025) occurred at site I in the winter. This value corresponded to those found in cities where the main contributor was coal combustion. These results are consistent with the fact that site T has a higher traffic density than site I and that PAH/NPAH emissions at site I were affected by coal burning from industrial activities. Site I, the Thuong Dinh industrial area, is the only old inner-city industrial zone remaining in the center of Hanoi city at that sampling time, which consumed 9.6 tons of coal per day.

Table 11.1 Diagnostic ratios of NPAHs and PAHs for various sources in Hanoi

Sample	[1-NP]/[Pyr][a]			[6-NB*a*P]/[B*a*P][a]	[7-NB*a*A]/[B*a*A][a]	IDP/B*ghi*Pe[a]
	Summer	Winter	Average			
Atm. (site I)	0.066 ± 0.075	0.025 ± 0.035	0.045 ± 0.055	0.004 ± 0.005	0.096 ± 0.158	0.83 ± 0.19
Atm. (site T)	0.145 ± 0.22	0.075 ± 0.098	0.110 ± 0.159	0.008 ± 0.005	0.065 ± 0.067	0.54 ± 0.14
Coal burning			0.001[b]		< 0.001 [d]	
Diesel engines			0.36[b]		0.14[b]	
Motor vehicles				0.008[c]		
Gasoline engines						0.4[d]
Diesel engines						1.0[d]

[a] All data show mean ± standard deviation
[b] Hayakawa (2009)
[c] Tang et al. (2012)
[d] Caricchia et al. (1999)
[e] Tang et al. (2005)

However, industrial activities of this area have now ceased. The concentration ratio of [6-NBaP]/[BaP] was 0.44×10^{-2} and 0.80×10^{-2} at sites I and T, respectively. These values were similar to the values found in Kanazawa, a typical automobile city in Japan (0.83×10^{-2} in the summer and 0.8×10^{-2} in the winter) and closer to the ratios for automobile exhaust from previous research (Tang et al. 2005; Hayakawa 2009), and are summarized in (Table 11.1). This result is reasonable because the combustion temperature of motorcycle engines is almost the same as that of motor vehicle engines (2700–3000 °C). The [7-NBaA]/[BaA] ratios were 0.096 and 0.065 at site I and site T, respectively, close to the ratio for automobile exhaust (0.14) and far from the ratio for coal-smoke combustion (<0.001), and further suggests that the main contributors to PAH and NPAH emissions in Hanoi were motor engines.

11.4 PAHs and NPAHs from Motorcycle Exhaust in Hanoi

Exhaust emitted from motorcycles contributes significantly to levels of air pollutants such as PAHs and NPAHs (Pham et al. 2012). An investigation on the contribution of motorcycles to atmospheric PAHs and NPAHs in a city dominated by motorcycles was conducted by measuring exhaust directly from motorcycle engines without catalytic converters. Exhaust emissions from ten in-use motorcycles with different engine capacities, different model years (2002–2010), and different manufacturers were tested. These vehicles were all equipped with four-stroke engines and without catalytic converters and were chosen because of their wide use in Hanoi. The test motorcycles were driven on an AVL-Zöllner chassis dynamometer (Kiel Prüfstand), which was located in the motorcycle test bed of the Internal Combustion

Engine Laboratory, at the Hanoi University of Science and Technology. The European driving cycle for motorcycle ECE R40 (Economic Emission for European Regulation 40) was used for the exhaust emission testing (Pham et al. 2013). The sampling temperature at the exhaust pipe was 165 °C or more and was reduced to 45–50 °C when diluted. PM was collected on Pallflex Emfab Filters (70 mm diameter) during the whole ECE 40 cycle phase. PAHs and NPAHs in PM were analyzed using the same procedure as described previously.

The PM emission factors for motorcycle exhaust in this study varied from 3.4 to 91.5 mg km^{-1}, and the average concentration of total 11 particulate phase PAHs in PM was 367.0 ± 315.7 μg km^{-1}. Among the ten tested motorcycles, emission factors of PM in exhaust (91 and 91.5 mg km^{-1}) from motorcycles with inadequate maintenance of the oldest engines (2002) were much larger than those for the newer motorcycles (model years from 2006 to 2010). The results of PM and PAH emissions from motorcycles were compared with those from automobiles obtained from previous studies (Robert et al. 2007; Riddle et al. 2007). PM emission rates per km driving from motorcycles were much larger than that from passenger cars (almost two orders of magnitude higher than that of low-emission automobiles). Even in comparison with automobiles, which were not equipped with catalytic converters, motorcycles emitted PM amounts about four times larger than automobiles. Compared with data regarding light-duty gasoline vehicles (Riddle et al. 2007), this study found that the total mass of five PAHs (Flu, Pyr, BaP, IDP, and B*ghi*Pe) emitted in PM from motorcycles was about 10 and 16 times higher than those from three-way catalyst equipped and low-emission automobiles, respectively. Detailed results of this comparison can be found in Pham et al. (2013).

In comparison to other diesel-engine automobiles (Yang et al. 2010), the current study found that, in general, the exhaust patterns of individual PAHs were similar between motorcycles and automobiles. However, the PAH concentrations in PM from motorcycles were much higher than those from diesel-engine automobiles by about two orders of magnitude (Fig. 11.6). In particular, the concentration of BaP, the most toxic compound among all PAHs, in PM from motorcycles was more than three orders of magnitude higher than that of PM from automobiles. Despite the smaller engine size of a motorcycle, this study showed that a motorcycle releases larger amounts of pollutants than an automobile suggesting the outsized contribution of motorcycles to PM and PAH emissions in airborne particulates in Hanoi.

In general, the concentration of particulate phase NPAHs from motorcycles was about three orders of magnitude smaller than those of corresponding PAHs. This study found that, among four NPAHs determined from motorcycle exhaust, 6-NC was in the highest abundance (73.1 ± 52.2 ng km^{-1}), followed by 7-NBaA and 1-NP (51.7 ± 50.9 ng km^{-1} and 44.9 ± 31.4 ng km^{-1}, respectively). Motorcycle engines fueled with gasoline emitted a lower level of 1-NP (by about ten times) as compared to automobile engines fueled with diesel (Fig. 11.7). These results are in agreement with the fact that 1-NP was the most abundant NPAH in diesel engine exhaust and exists in much higher levels, compared to gasoline engine vehicles (Scheepers et al. 1995; Tang et al. 2005; Hayakawa et al. 2007). The results also showed that motorcycle engines fueled with gasoline exhausted lower levels of 1-NP and a

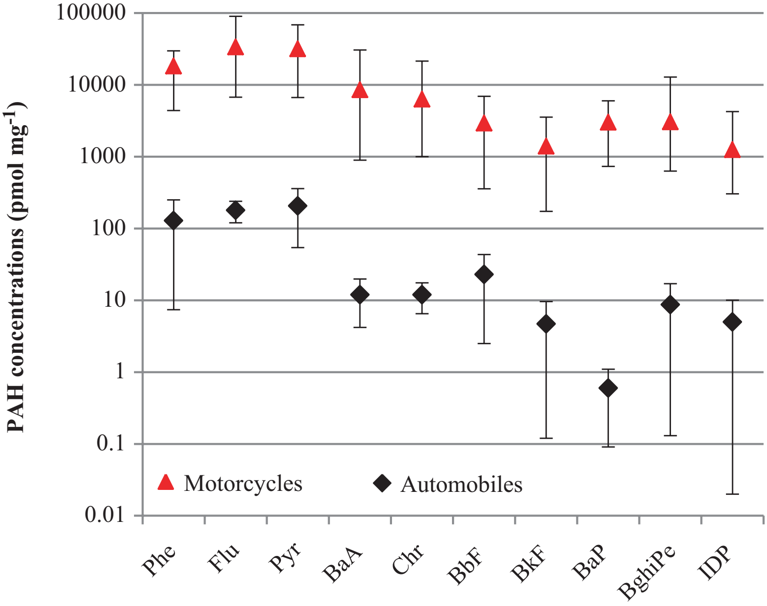


Fig. 11.6 Comparison of individual PAHs in PM between motorcycles and automobiles
Data of automobile exhausts cited from a previous report (Yang et al. 2010)
Data show the averages and minimum and maximum values of PAHs

considerably higher level of BaP and 6-NBaP, as compared to automobile engines fueled with diesel. This difference may be associated with the different compositions of gasoline and diesel fuels and/or different engine types under different operating conditions (Dennis and Joseph, 1983). This finding is useful in understanding the composition of the toxic compounds found in motorcycles.

It is well known that many PAHs and NPAHs are carcinogenic and mutagenic compounds. The mutagenic properties and potential carcinogenicity for some PAHs and NPAHs have been documented in a report by the International Agency for Research on Cancer (IARC 2010). Yang et al. (2010) assessed the carcinogenicity and indirect-acting mutagenicity of individual PAHs and direct-acting mutagenicities of individual NPAHs in PM from motorcycle exhaust using a toxic equivalent factor (TEF) approach and Ames testing (Nisbet and Lagoy 1992; Yang et al. 2010). A BaP_{eq} factor was calculated for each individual PAH by multiplying its concentration in PM with its corresponding TEF. The study found that the carcinogenic potencies of 11 PAHs from motorcycles were more than two orders of magnitude higher than those from automobiles (Table 11.2). This reflects the much higher PAH emissions, including BaP, from motorcycles than from automobiles. The results also show that PM extracts from motorcycles exhibited much higher indirect-acting mutagenic potency (about 200 times) than those from automobiles. However, the direct-acting mutagenicity of total NPAHs from motorcycles was about ¼ of that from automobiles (Table 11.2). This is due to the large contribution of 1-NP, which

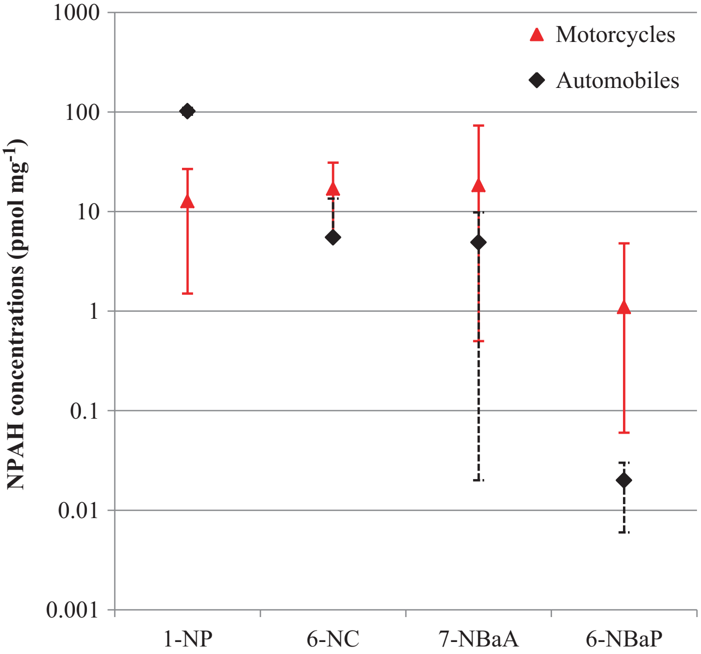


Fig. 11.7 Comparison of individual NPAHs in PM between motorcycles and automobiles
Data of automobile exhaust cited from a previous report (Yang et al. 2010)
Data show the averages and minimum and maximum values of NPAHs

is the most toxic NPAH in diesel exhaust. The study concluded that despite a small engine size, motorcycles emitted much more PM and PAHs and showed stronger PAH-related carcinogenicity and indirect-acting mutagenicity but weaker NPAH-related direct-acting mutagenic potency than automobiles.

11.5 Relationship Between PAH/NPAH Concentrations in Soil and Airborne Particulates

The soil is an important sink for atmospheric PAH deposition. After long-range transport in the atmosphere, most PAHs accumulate in soil through atmospheric deposition (Gocht et al. 2007). NPAHs are also important environmental pollutants because they are more toxic than PAHs and strongly accumulate in sediment (Furlong and Carpenter 1982; Osborne et al. 1997). While exhaust from traffic vehicles, especially motorcycles, are a major contributor to atmospheric PAHs and NPAHs in Hanoi city (Pham et al. 2012), we continued to investigate the occurrence of PAHs and NPAHs in soil and the relationship between atmospheric particles and soil at traffic sites in Hanoi.

Table 11.2 Toxicity of individual PAH and NPAHs in PM exhausted from motorcycles and automobiles

Component	A. Carcinogenicity (BaP_{eq}, µg g^{-1})		B. Indirect mutagenicity (rev. g^{-1})	
	Motorcycle	Automobile	Motorcycle	Automobile
Phe	3.3 ± 1.5	0.02 ± 0.03	< 18,341	< 129
Ant	7.3 ± 3.8	ND	< 4103	ND
Flu	6.8 ± 5.1	0.04 ± 0.02	337,674 ± 263,582	1800 ± 850
Pyr	6.4 ± 4.1	0.04 ± 0.04	< 31,688	< 207
BaA	194.7 ± 199.4	0.27 ± 0.25	85,282 ± 90,427	120 ± 110
Chr	14.4 ± 13.7	0.03 ± 0.02	< 6316	< 12
BbF	74.0 ± 60.9	0.58 ± 0.73	99,742 ± 86,920	782 ± 986
BkF	35.4 ± 28.1	0.12 ± 0.23	21,051 ± 17,641	705 ± 1380
BaP	759.4 ± 497.1	0.15 ± 0.33	192,627 ± 117,868	38 ± 83
BghiPe	8.4 ± 10.0	0.02 ± 0.00	3052 ± 1241	9 ± 18
IDP	34.7 ± 31.8	0.14 ± 0.20	3764 ± 1479	15 ± 21
C. Direct mutagenicity (rev. g^{-1})				
1-NP	3822 ± 2352	30,600 ± 3300		
6 –NC	< 1699	< 550		
7- NBaA	< 1844	< 490		
6- NBaP	< 110	< 2		

Data of automobile exhausts cited from previous report (Yang et al. 2010)
Each data means average ± standard deviation
ND: not detected

Soil samples were collected at four sites (HB1, HB2, MT1, MT2) within 500 m from air sampling site (site T, heavy traffic area) (Fig. 11.1). At each site, soil samples were taken from three different depths (0–5, 5–10, 15–20 cm). The collected samples were air-dried in a fume hood at room temperature for 6 days, ground and screened through a 600 µm sieve, transferred to glass bottles, and stored at −20 °C until use. PAHs and NPAHs in soil were extracted ultrasonically twice with 40 ml benzene/ethanol (3:1, v/v) for 20 min each. More detailed information can be found in Pham et al. (2015).

The total concentration of the ten PAHs examined in soil near the traffic areas varied between 3.4 and 43.7 ng g^{-1} dry weight. The concentration order of the predominant PAHs (high-molecular-weight PAHs such as B*ghi*Pe and B*b*F) in soil was similar to that found in airborne particulates (TSP). PAHs in soil may undergo transformation through processes such as biodegradation, evaporation, and photochemical reaction. The lower the molecular weight or number of condensed rings, the greater the likelihood of degradation by soil microbes or through evaporation. Therefore, these results suggest that the higher molecular weight PAHs in soil were most likely deposited from the atmosphere.

There are two reasons to assume that PAH burden in soil is a reflection of accumulative deposition from the atmosphere: the concentration ratios of NPAHs with their parent PAHs and the ratios of [BaA]/([BaA] + [Chr]). The order of the values of the three pairs, [6-NBaP]/[BaP], [7-NBaA]/[BaA], and [1-NP]/[Pyr], in soil was

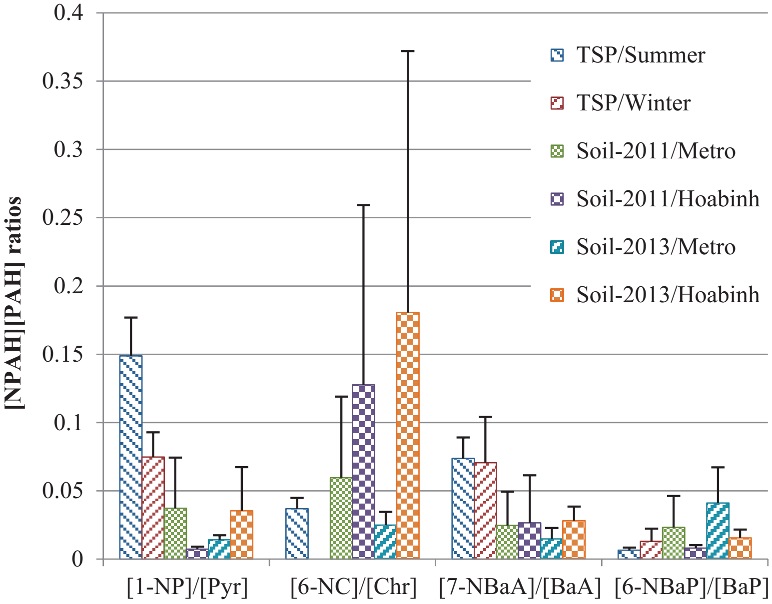


Fig. 11.8 Comparison of [NPAHs]/[PAHs] ratios between soil and TSP
Data of the [NPAHs]/[PAHs] ratios for TSP show the average values in winter and summer
Data of the [NPAHs]/[PAHs] ratios for soil show the average values at HB1, HB2, MT1, MT2 soil sites in 2011 and 2013

the same range with that in TSP, suggesting the same emission sources of PAHs and NPAHs between the soil and atmosphere (Fig. 11.8). In addition, the ratios of [BaA]/([BaA] + [Chr]) in soil in the present study varied between 0.47 and 0.80. Since these ratios were above 0.35, this indicates that the pollution is from combustion sources (Ma et el. 2008). This indicates that PAHs present in soil originate primarily from atmospheric combustion emissions. As described above, 6-NC was the most abundant NPAH among 4 NPAHs determined from motorcycle exhaust. 6-NC from motorcycle exhaust may easily deposit onto the soil, rather than enter the atmosphere. The mean concentration ratios of [6-NC]/[Chr] in soil were considerably higher than those in TSP. There are three possible reasons that need to be considered: (i) the higher stability or lesser mobility of 6-NC in soil, (ii) the slow biodegradation of 6-NC, and (iii) 6-NC is secondarily formed in soil. 6-NC in soil is expected to have no mobility based on an estimated soil adsorption partition coefficient (K_{oc}) of 2.9×10^5, determined through a structure estimation method. 1-NP also is expected to be immobile in soil but with a lower K_{oc} value of 1.35×10^4 (Swann et al. 1983; Boethling and Mackay 2000; Meylan et al. 1982). Heitkamp et al. (1988) assayed mineralization of some PAHs after 2 weeks of incubation with a PAH-degrading bacterium and found that the percentage of mineralized PAH was more than 50% for two- and three-ring PAHs but only 12.3% for 1-NP and 2.0% for 6-NC (Heitkamp et al. 1988; Heitkamp and Cerniglia 1988).

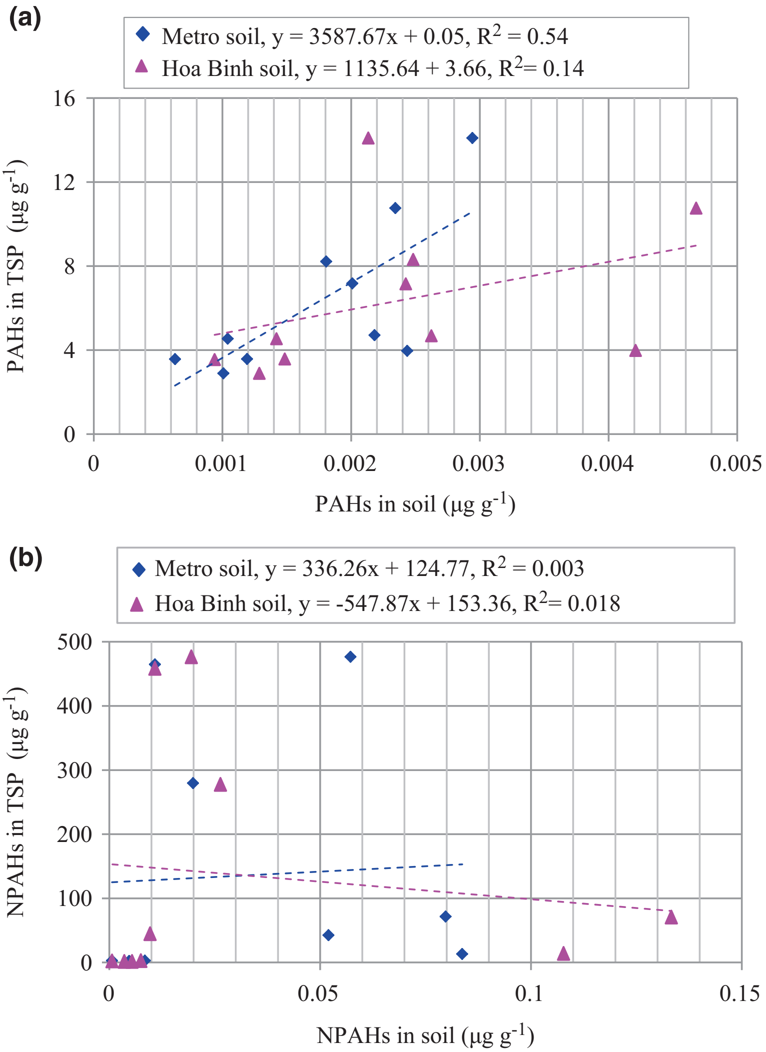


Fig. 11.9 Relation of (**a**) PAH and (**b**) NPAH concentrations between soil and TSP

This study showed that the PAH levels in airborne particulates (TSP) were positively correlated with those in soil ($R^2 = 0.54$ and 0.14). However, the NPAH levels in the TSP and soil samples were not correlated at two sites (Fig. 11.9). This correlation coefficient is further evidence that PAHs in the atmosphere are deposited in soil and relatively stable. However, the source and stability of NPAHs in soils remains unclear.

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Chapter 12
Emission Sources of Polycyclic Aromatic Hydrocarbons/Nitropolycyclic Aromatic Hydrocarbons in Cairo, Egypt, Including Source Markers

Hossam F. Nassar

Abstract Polycyclic aromatic hydrocarbons (PAHs) are produced in the environment as by-products of the incomplete combustion of most fuels. Therefore, they are ubiquitous in the environment and particularly concentrated in urban and industrialized areas (Mastral and Callén 2000; Rehwagen et al. 2005; Nassar et al. 2011; Li et al. 2012) and are widely studied with regard to their environmental effects due to their well-known carcinogenic and mutagenic properties. PAHs are emitted into the atmosphere through various combustion sources or released into the aquatic environment through industrial discharge or domestic sewage.

Keywords PAHs · NPAHs · Ismailia Canal · Egypt · NPAH/PAH ratios

Polycyclic aromatic hydrocarbons (PAHs) are produced in the environment as by-products of the incomplete combustion of most fuels. Therefore, they are ubiquitous in the environment and particularly concentrated in urban and industrialized areas (Mastral and Callén 2000; Rehwagen et al. 2005; Nassar et al. 2011; Li et al. 2012) and are widely studied with regard to their environmental effects due to their well-known carcinogenic and mutagenic properties. PAHs are emitted into the atmosphere by various combustion sources or released into the aquatic environment through human activity discharge such as through industrial or domestic sewage effluent.

PAHs are a widespread class of environmental pollutants and are among the most carcinogenic, mutagenic, and toxic contaminants found in aquatic systems (Kakimoto et al. 2000; Nassar et al. 2011). There are several possible sources for PAHs in the environment. Two classes of PAH inputs are through natural processes and anthropogenic activities, but the latter is generally considered to be the major

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source of PAH inputs into the environment. Although some PAHs are naturally occurring, the majority are anthropogenic and enter the environment through the release of petroleum products (petrogenic sources) or through the combustion of organic matter (pyrogenic sources) both of which have different environmental availabilities (Burgess et al. 2003; Nassar et al. 2015). Recent studies have shown that pyrogenic sources dominate in urban settings and that the PAH profiles in urban storm water resemble that of atmospheric deposition (Tang et al. 2005; Li et al. 2012).

In recent years, several diagnostic ratios and multivariate statistical analysis methods have been used to identify possible emission sources of PAHs and their nitrated derivatives (NPAHs) in the atmosphere (Bourotte et al. 2005; Hattori et al. 2007). Molecular diagnostic ratios of several PAHs have been used to identify their sources, including diesel and gasoline engine vehicles. Based on their results, two ratios of [benz[*a*]anthracene]/[chrysene] ([BaA]/[Chr]) and [benzo[*ghi*]perylene]/[benzo[*a*]pyrene] ([BghiPe]/[BaP]) could distinguish gasoline from diesel exhausts.

Egypt is growing not only in population and number of vehicles but also in industrial activity. Urbanization and industrialization have increased very rapidly in Egypt, particularly in the second half of the last century, causing an increase in the pollution of its air-water environment (Nasr et al. 2009). Nassar et al. (2011) studied PAHs and selected NPAHs in the atmosphere at two sites in Egypt: El Dokki (a traffic site) and El Teppen (an industrial site) in Greater Cairo, Egypt, during the winter and summer seasons. The sites were selected to represent areas with different activities. In this study, the [BaA]/[Chr] ratio ranged from 0.69 in the summer to 0.5 in the winter, and the [BghiPe]/[BaP] ratio ranged from 0.58 in summer to 1.15 in winter, suggesting a relatively stronger contribution of gasoline engine vehicles at both El Dokki and El Teppen sites. On the other hand, the much lower combustion temperature in coal stoves (approximately 1100–1200 °C) than in diesel engines (approximately 2700 °C) was considered the cause of the lower ratio of mono-NPAH to its parent PAH in coal stoves (Hattori et al. 2007). The contributions of diesel exhaust particulate (DEP) and coal-burning exhaust particulate (CEP) were estimated from their [1-nitropyrene]/[pyrene] ([1-NP]/[Pyr]) ratios. These ratios showed that in several East Asian cities, DEP was the major contributor in Japanese and Korean commercial cities (Tokyo, Sapporo, Kanazawa, and Seoul) and that CEP was the major contributor in Chinese and Russian cities (Shenyang and Vladivostok) and a Japanese industrial city (Kitakyushu) (Tang et al. 2005). In the present study, the [1-NP]/[Pyr] ratio was 0.03 and the [6-nitrochrysene]/[Chr] ([6-NC]/[Chr]) ratio was 0.01 in summer, while the [1-NP]/[Pyr] ratio ranged between 0.005 and 0.006 and the [6-NC]/[Chr] ratio was 0.001 in winter at both sites. By comparing these results with those of East Asian cities, we found that summer [1-NP]/[Pyr] ratios at both sites were higher than those of East Asian cities except Kanazawa and [6-NC]/[Chr] ratios at both sites were almost the same as those of East Asian cities except Kanazawa. Winter [1-NP]/[Pyr] ratios at both sites were higher than those of East Asian cities, and [6-NC]/[Chr] ratios were almost the same with Kanazawa and Vladivostok and lower than in Shenyang and Beijing (Table 12.1).

Table 12.1 A comparison of [NPAH]/[PAH] concentration ratios at East Asian cities and in Greater Cairo

	Winter		Summer	
City	[1-NP/Pyr]	[6-NC/Chr]	[1-NP/Pyr]	[6-NC/Chr]
Shenyang	1×10^{-2}	6×10^{-3}	2×10^{-2}	1×10^{-2}
Beijing	5×10^{-3}	5×10^{-3}	2×10^{-2}	1×10^{-2}
Vladivostok	1×10^{-2}	1×10^{-2}	2×10^{-2}	1×10^{-2}
Kanazawa	3×10^{-2}	1×10^{-2}	7×10^{-2}	4×10^{-2}
Cairo T	6×10^{-3}	1×10^{-3}	3×10^{-2}	1×10^{-2}
Cairo D	5×10^{-3}	1×10^{-3}	3×10^{-2}	1×10^{-2}

Another report assessed PAH and NPAH concentrations at the Nile River and Ismailia Canal in Egypt (Nassar et al. 2015). Freshwater samples at three sites in the Nile River (NR1, NR2, and NR3) and two sites in the Ismailia Canal (E1 and E2) in Egypt were collected. The first site was in Greater Cairo at the intake of a drinking water treatment plant. At this location, the electrical power station, ship maintenance center, and Nile transportation discharged their wastewater into the River. This site is considered downstream to most Greater Cairo activities (NR1). The second site was Banha (North Egypt) in the north part of Nile River at the beginning of the delta area. This was a residential site affected mainly by agricultural waste loaded with different chemicals and toxic organic nutrients (NR2). The third site was Beni-Suef (Upper Egypt) in the south part of River Nile (NR3). This site was affected by urbanization, traffic, and some industries like cement and fertilizer facilities.

The Ismailia Canal water is very polluted especially in the first 10 km in the Greater Cairo area, due to the large presence of industry and oil companies. Two sites were selected along the Ismailia Canal. The first site (E1) was located 10 km from the beginning of the canal and so is affected only by urban activity and traffic emissions. The other site (E2) was located 5 km from the beginning of the canal and is affected by several kinds of pollutants from different factories such as paper, food, petroleum, and petroleum derivative industries that discharge their untreated wastewater into the Ismailia Canal.

The most widely used diagnostic ratios are [fluoranthene]/[Pyr] ([Frt]/[Pyr]), [Frt]/[Pyr + Frt], [1-NP]/[Pyr], and [6-NC]/[Chr]. This is the first report to discuss the PAH and NPAH sources in the Egyptian water environment. We compared the molecular diagnostic ratios of the water sites in this study with atmospheric sites in El Dokki and El Teppen from our previous study (Nassar et al. 2011). A [Frt]/[Frt + Pyr] ratio of <0.4 indicates a petrogenic source, while [Frt]/[Frt + Pyr] > 0.4 indicates crude oil and/or wood/grass/coal combustion sources (Budzinski et al. 1997; Brandli et al. 2007). For the Nile River sites (NR1, NR2, and NR3), [Frt]/[Frt + Pyr] were around 0.3–0.4 in both summer and winter seasons, indicating a mainly petrogenic source contribution in both seasons, whereas for Esmailia canal sites (E1 and E2), those ratios were around 0.6–0.7, indicating a mixed source contribution (Table 12.2).

Table 12.2 Molecular diagnostic ratios at sampling sites (El Dokki and El Teppen) and water sampling sites (NR1, NR2, NR3, E1, and E2) in summer and winter seasons

		Winter				Summer			
Sample	Site	[Frt]/[Pyr]	[Frt]/[Frt + Pyr]	[1-NP]/[Pyr]	[6-NC]/[Chr]	[Frt]/[Pyr]	[Frt]/[Frt + Pyr]	[1-NP]/[Pyr]	[6-NC]/[Chr]
Airborne	[a]Dokki	0.9	0.5	5×10^{-3}	1×10^{-3}	0.8	0.3	3×10^{-2}	3×10^{-2}
	[a]Teppen	1.7	0.6	6×10^{-4}	1×10^{-3}	1.4	0.7	3×10^{-2}	1×10^{-2}
Water	[b]NR1	0.8	0.3	3×10^{-3}	3×10^{-2}	0.8	0.4	2×10^{-3}	2×10^{-2}
	[b]NR2	0.6	0.3	4×10^{-3}	11×10^{-2}	0.7	0.1	3×10^{-3}	12×10^{-2}
	[b]NR3	0.8	0.4	4×10^{-3}	8×10^{-2}	0.9	0.4	3×10^{-4}	17×10^{-2}
	[b]E1	1.6	0.6	6×10^{-4}	4×10^{-3}	1.3	0.6	1×10^{-3}	1×10^{-2}
	[b]E2	2.6	0.6	7×10^{-3}	4×10^{-3}	1.9	0.8	2×10^{-3}	1×10^{-2}

[a] Airborne particulate sampling site

[b] water sampling site

The concentration ratios of mono-NPAHs to their corresponding PAHs such as [1-NP]/[Pyr] and [6-NC]/[Chr] were effectively used to investigate the source origin in the following increasing order: wood burning particulates < CEP < DEP (Tang et al. 2005). The [1-NP]/[Pyr] for the Nile River sites ranged from 3×10^{-3} to 4×10^{-3} and from 3×10^{-4} to 2×10^{-3} in the summer and winter seasons, respectively. The relatively lower values in Ismailia Canal sites over the Nile River sites indicated a mixed contamination of CEP with petroleum sources at the Ismailia Canal and petrogenic sources contaminated with CEP (open-air burning) inputs at the Nile River sites. [Frt]/[Pyr] ratios were used to differentiate between pyrogenic and petrogenic sources (Budzinski et al. 1997; Soclo et al. 2002). Sicre et al. (1987) found that a [Frt]/[Pyr] < 1 was attributed to petrogenic sources, and values greater than 1 were related to a pyrolytic origin. [Frt]/[Pyr] values for the Nile River sites were slightly lower than 1 indicating a combined contamination of petrogenic origin and pyrogenic sources with petrogenic sources dominant at River Nile sites. This is in contrast with Ismailia Canal site [Frt]/[Pyr] values which were slightly higher than 1, indicating a predominance of pyrogenic source origin contaminated with petrogenic sources at Ismailia Canal sites. These values are in agreement with our abovementioned investigations.

Since the abundance of high molecular weight (HMW), PAH (e.g., 5 and 6 rings) species is typically characteristic of pyrogenic origins, while low molecular weight (LMW) PAHs (e.g., two- and three-ring species) are more abundant in petroleum sources, ratios of LMW/HMW PAHs were calculated to further distinguish petroleum from combustion source inputs. LMW/HMW ratios >1 indicate a petroleum source, while values <1 imply a combustion source (Walker et al. 2005; Nassar et al. 2012).

In this study, the concentration ratios of [LMW]/[HMW] PAHs and NPAHs in summer and winter seasons were >1, indicating an abundance of LMW PAHs and petrogenic source contamination (Table 12.3), but also there were considerable amounts of HMW compounds indicating inputs from both petrogenic and pyrogenic sources as a combined origin (Fig. 12.1). These results are in agreement with Chen et al. (2005) and Aichner et al. (2007).

Table 12.3 Percentage of LMW, MMW, and HMW PAH compounds at the Nile River and Ismailia Canal sites in summer and winter seasons

Comp	NR1				NR2				NR3				E1				E2			
	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%
PAHs																				
LMW	2201.5	89	28326	88	875.0	88	1092.9	86.	1065.4	89	1284.3	90	5146.7	83	6220.7	81	10810	85	14026.0	81
MMW	207.0	8	256.1	7	90.2	10	135.3	11	109.6	9	106.5	7	897.2	14	1139.0	16	1625.3	12	2739.0	14
HMW	62.4	3	115.0	5	23.3	2	33.7	3	14.6	1	37.1	3	124.9	3	187.3	3	236.1	3	509.2	5
NPAHs																				
LMW	4.96	65	6.80	63	3.14	60	4.50	65	3.39	61	5.28	66	4.11	61	8.05	68	9.42	59	11.06	55
MMW	2.58	34	3.94	36	2.00	40	2.48	35	2.20	39.	2.58	33	2.65	38	3.70	31	6.43	41	9.00	44
HMW	0.08	1	0.06	1	0.03	0	0.03	0	0.05	0	0.05	1	0.03	1	0.07	1	0.09	0	0.20	1

LMW, 2-3 ring; MMW, 4-5 ring; HMW, 6- ring

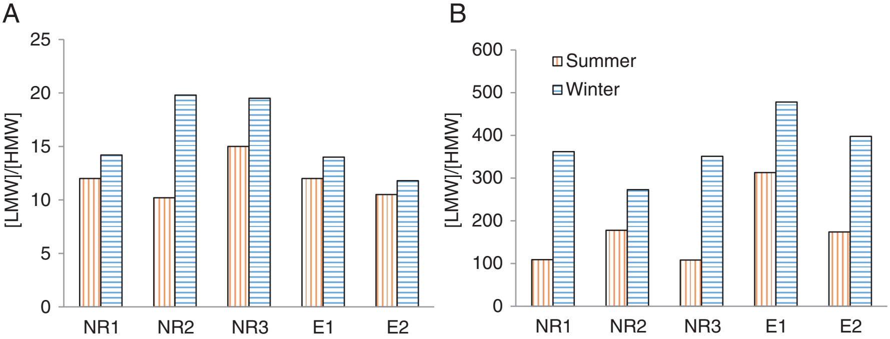

Fig. 12.1 Comparison of [LMW]/[HMW] ratios of PAHs and NPAHs at the Nile River and the Ismailia Canal sites in the summer and winter (A) PAHs, (B) NPAHs
LMW PAHs = Nap, Ace, Fle, Ant, Phe, Frt, Pyr, BaA, and Chr
HMW PAHs = BbF, BkF, BaP, Bghipe, and IDP
LMW NPAHs = 2-NF, 9-Nph, 9-NA, 3-NFR, 1-NP, 6-NC, and 7-NBaA
HMW NPAHs = 6-NBaP

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Chapter 13
Model Simulations of PAHs in Northeast Asia

Yayoi Inomata

Abstract The emissions, concentrations, and transboundary transport of particulate polycyclic aromatic hydrocarbons (PAHs) in Northeast Asia were investigated using Regional Emission inventory in Asia for Persistent Organic Pollutants (REAS-POP) and the chemical transport model (Regional Air Quality Model for POPs version, RAQM-POP). The nine particulate PAH concentrations simulated agreed well with the measured concentrations, and the results firmly established the efficacy of REAS/RAQM-POP. The estimated annual emission of the nine PAHs in 2005 in Northeast Asia was approximately 10.5 Gg year^{-1}, and the emission from China (9.6 Gg year^{-1}) accounted for 92% of emissions in Northeast Asia. The largest component of these emissions was four-ring PAHs, followed by five- and six-ring congeners. It was found that the PAH concentrations in Beijing, which were emitted predominantly from domestic coal, domestic biofuel, and coke production, were approximately two orders of magnitude greater than those at Noto (in Japan, leeward region). In Noto, the PAH concentrations showed seasonal variations with highs from the winter to spring and lows in the summer. These seasonal variations were due to seasonal variations in emissions from China, as well as transboundary transport across the Asian continent. Also, in the summer, the contribution from domestic sources such as on-road automobiles showed a relative increase.

Keywords PAH · Northeast Asia · Emission inventory · Chemical transport model · Transboundary transport

13.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) have a high carcinogenic potential in humans, and the major routes of exposure are through inhalation and their bioaccumulation in the food chain (ATOSDR 1995). Particulate-bound PAHs can be transported

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over long atmospheric distances and result in their widespread worldwide distribution. Although measurements of particulate PAHs have been conducted by many (e.g., Yang et al. 2007; Hattori et al. 2007; Zhang et al. 2009), these studies are limited in their elucidation of the transboundary transport of PAHs in Northeast Asia. To evaluate pollution levels and transboundary transport of PAHs in Northeast Asia, it is necessary to investigate the temporal and spatial variations of PAHs using a chemical transport model. In this chapter, spatial and temporal distributions of PAHs in Northeast Asia are described by using the Regional Air Quality Model for Persitrent Organic Pollutants (RAQM-POP; Inomata et al. 2012; Kajino et al. 2012) and PAH emission inventory for Northeast Asia, applying the Regional Emission inventory in ASia (REAS, Ohara et al. 2007) to POPs inventory (REAS-POP). The temporal variations of the nine PAH concentrations measured in Beijing, China (source region), and Noto, Japan (leeward region), were interpreted using the model simulation.

13.2 Emission Inventory of PAH

The REAS-POP in Northeast Asia includes emission data for 16 PAHs (two rings, naphthalene (NaP); three rings, acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), and anthracene (Ant); four rings, fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), and chrysene (Chr); five rings, benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), and dibenz[*a,h*]anthracene (DBahA); and six rings, indeno[1,2,3-*cd*]pyrene (IcdP) and benzo[*g,h,i*]perylene (BghiP)) that are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) (USEPA 2003). The available measurement data used to validate REAS-POP was limited to nine PAHs (Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, and BghiP) because volatile PAHs that contain two or three rings could not be recovered during the collection of airborne particulates. The monthly emission of each PAH species was estimated by the multiplication of the emission factor and the fuel consumption rate. The horizontal resolution is gridded at 0.5° × 0.5°, and the period is from 2000 to 2005.

Figure 13.1 shows the geographical distribution of the annual emissions of the nine PAHs at a resolution of 0.5° × 0.5° in Northeast Asia in 2005 (RAQM-simulated domain; longitude 84–161°E, latitude 16–55.5°N). China was shown to be the most significant contributor of the nine PAHs in Northeast Asia. In particular, the elevated levels of nine PAHs are noted in Northern Central China, the North China Plain, the east coast of China, Guizhou, Sichuan Basin, and Northeast China. The estimated annual emission of the nine PAHs in China in 2005 was approximately 9.6 Gg year^{-1}, which accounted for 92% of the total emissions (10.5 Gg year^{-1}) in Northeast Asia in 2005. According to a previously reported study (Xu et al. 2006), the total 2003 emissions of the nine PAHs in China was estimated to be 7.1 Gg year^{-1}. This estimation was similar to ours (8.0 Gg year^{-1}) for 2003. The emission from the eastern part of Russia was estimated at 0.19 Gg year^{-1} (1.8% of the total emission of the 9 PAHs in Northeast Asia), North Korea as 0.29 Gg year^{-1} (2.7%), Mongolia

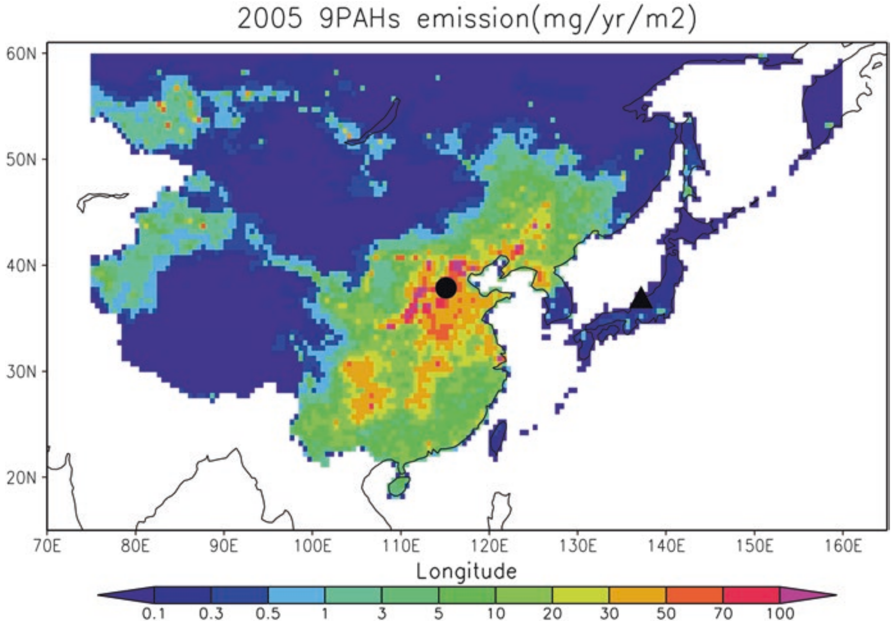

Fig. 13.1 Spatial distributions of the annual emissions of nine PAHs at a 0.5 × 0.5 resolution in 2005 in Northeast Asia. The scale is in the units of mg year^{-1} m^{-2}. ● indicates the location of Beijing, and ▲ indicates the location of Noto

as 0.021 Gg year^{-1} (0.20%), Japan as 0.020 Gg year^{-1} (0.19%), South Korea as 0.020 Gg year^{-1} (0.29%), and Taiwan as 0.0028 Gg year^{-1} (0.0036%).

Figure 13.2 shows the emission of individual PAHs from various sources in Northeast Asia in 2005. This data was used as it could be validated based on measured data. The estimated emissions and their percentage of the total emissions of the 9 PAHs is as follows: 2.2 Gg year^{-1} (21%) for Flu, 1.9 Gg year^{-1} (18%) for Pyr, 0.90 Gg year^{-1} (9%) for BaA, 0.93 Gg year^{-1} (9%) for Chr, 1.4 Gg year^{-1} (13%) for BaP, 1.4 Gg year^{-1} (13%) for BbF, 0.52 Gg year^{-1} (5%) for BkF, 0.59 Gg year^{-1} (6%) for BghiP, and 0.75 Gg year^{-1} (7%) for IcdP. The highest emissions were from Flu, which contains four benzene rings, followed by Pyr (four rings), BbF (five rings), and BaP (five rings).

Although the emission profile for each country is not shown here, the emission profiles shown in Fig. 13.2 reflect the emission patterns from China because it is the dominant source of PAHs in Northeast Asia. The emission profiles of the nine PAHs vary considerably from county to country. In China, the dominant PAH sources were domestic coal (47%), domestic biofuel (18%), and other coal combustion sources including coke production (29%). In the eastern part of Russia, North Korea, and Mongolia, domestic biofuel (4% for the eastern part of Russia, 33% for North Korea, and 43% for Mongolia), domestic coal (28% for the eastern part of Russia, 61% for North Korea, and 11% for Mongolia), and other coal transformation

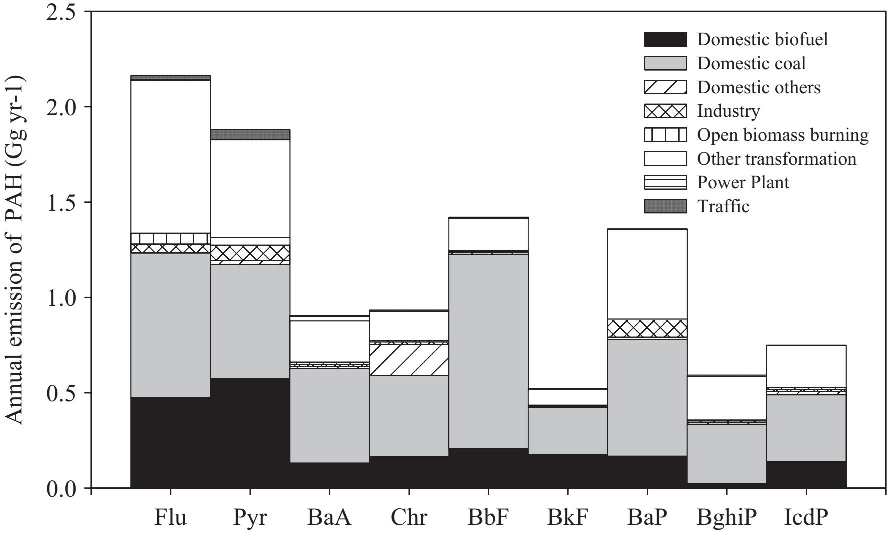

Fig. 13.2 Annual emissions of the nine PAHs in Northeast Asia from various emission sources in 2005

products (37% for the eastern part of Russia, 3% North Korea, and 4% for Mongolia) were also dominant sources. Furthermore, the emission from open biomass burning was also a large contributor in the eastern part of Russia (31%) and Mongolia (38%). In Japan and Taiwan, the major emission source was on-road vehicles, accounting for 68% and 44% of their respective PAH emissions. These results are consistent with those found using a cluster analysis and factor analysis, which were based on measurement data and demonstrated that the main source of PAHs in Japanese cities (Kanazawa, Tokyo, and Sapporo) was automobiles, especially diesel-engine vehicles (Tang et al. 2005). The South Korean emissions originated primarily from on-road vehicles (35%), industry (32%), other coal transformation products (15%), and domestic coal (11%).

Figure 13.3 shows the seasonal variation of the monthly BaP emissions (which is selected specifically, since it is highly toxic) in Northeast Asia in 2005. The monthly BaP emissions showed a clear seasonal variation; the levels were high in the winter-spring and low in the summer (Fig. 13.3(1)). This seasonal variation was derived from domestic coal and domestic biofuel sources. The relative contributions from domestic biofuel and domestic coal increased in the winter season due to the use of heating systems. Conversely, the relative contribution of the other coal transformation products increased in the summer (Fig. 13.3(2)). For the other eight PAHs, the seasonal variation and relative contribution from each source were similar to those of BaP.

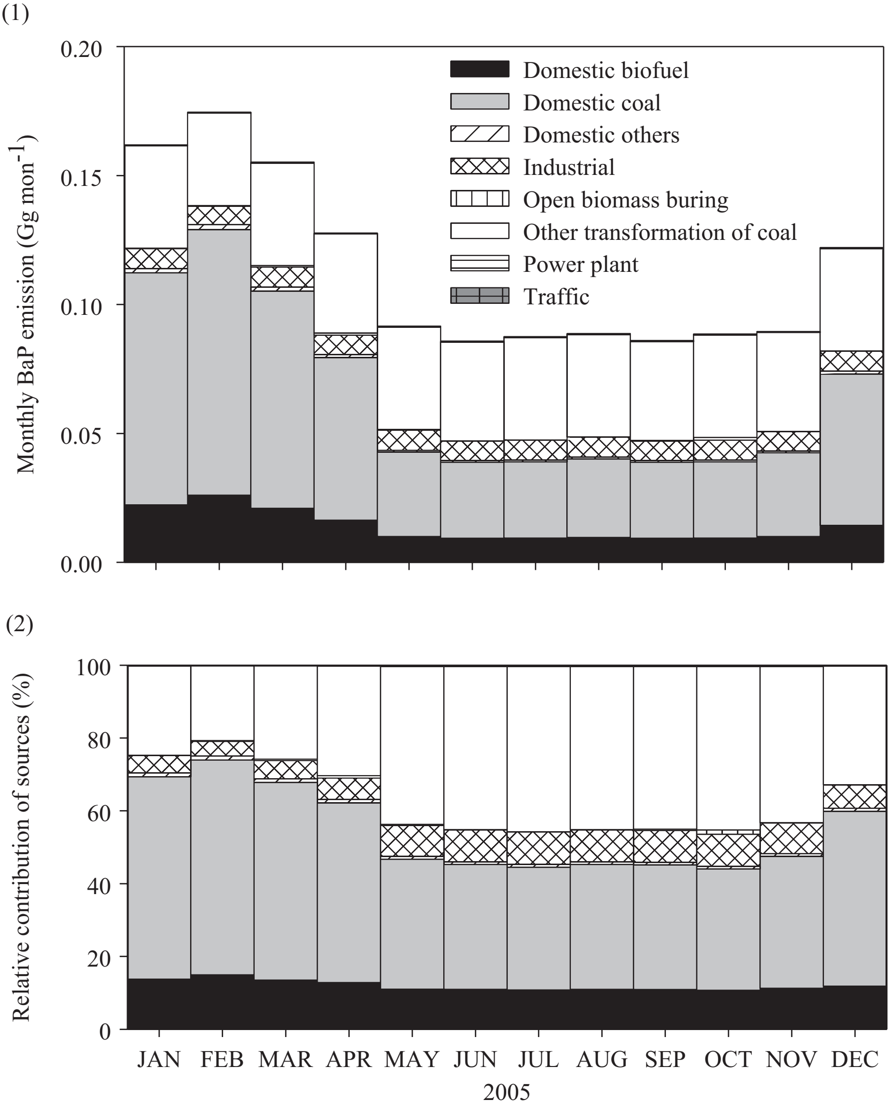

Fig. 13.3 Seasonal variations of (1) monthly BaP emissions and (2) the relative contributions of various sources to BaP emission in Northeast Asia in 2005

13.3 Seasonal Variation of Measured and Simulated PAH Concentrations at the Beijing and Noto Monitoring Sites

The RAQM, a three-dimensional Eulerian chemical transport model, was used to simulate the PAHs. The Weather Research and Forecasting (WRF; model version 3.0) was used to provide a meteorological field for RAQM-POP. The RAQM-POP model domain covers most areas of the Northeast Asian countries. The horizontal grid resolution is 60 km with a Lambert conformal map projection, and there are 12 layers from the ground to 10 km. The data (concentrations, wet depositions, and dry depositions) were recorded on an hourly basis.

Figure 13.4 shows the temporal variation of measured and simulated particulate PAH concentrations at the Beijing (China, longitude 116.4°E, latitude 40.0°N) and Noto (coastal site of Sea of Japan in Japan, longitude 136.9°E, latitude 37.5°N) monitoring sites. At both sites, the simulated PAH concentrations generally agreed with the quantitatively measured concentrations. In Beijing, concentrations of PAH showed a daily variation and gradually decreased from winter to spring. In the case of Noto, PAH concentrations showed clear seasonal variation with high concentrations in the autumn-winter and low in the summer. It appeared that the PAH concentrations in Beijing were two orders of magnitude larger than those at Noto.

Figure 13.5 shows the horizontal distributions of the simulated weekly average particulate BaP concentrations and wind vectors near the surface when maximum (21–28 January 2005) and minimum PAH concentrations (9–16 July 2005) were observed in Noto (see Fig. 13.4). Again, BaP was selected as a surrogate for the characterization of nine PAHs because of its high toxicity. As shown in Fig. 13.5 (1), high BaP concentrations were observed over a wide region in China from 21–28 January, and we can observe the transboundary transport of BaP from the Asian continent toward the Japanese islands. Northwesterly winds prevailed over Northeast Asia during the observation period, which suggests that BaP would be advected from Northeast Asia to the Japanese islands. In contrast, as shown in Fig. 13.5 (2), southerly and southwesterly winds prevailed over the Pacific Ocean from 9–16 July due to the Pacific High pressure system. The transboundary transport of BaP from the Asian continent would be prevented by the Pacific High.

These results suggest that the seasonal variations in BaP emissions (as shown in Fig. 13.3) and the prevailing meteorological conditions strongly controlled transboundary transport in Northeast Asia.

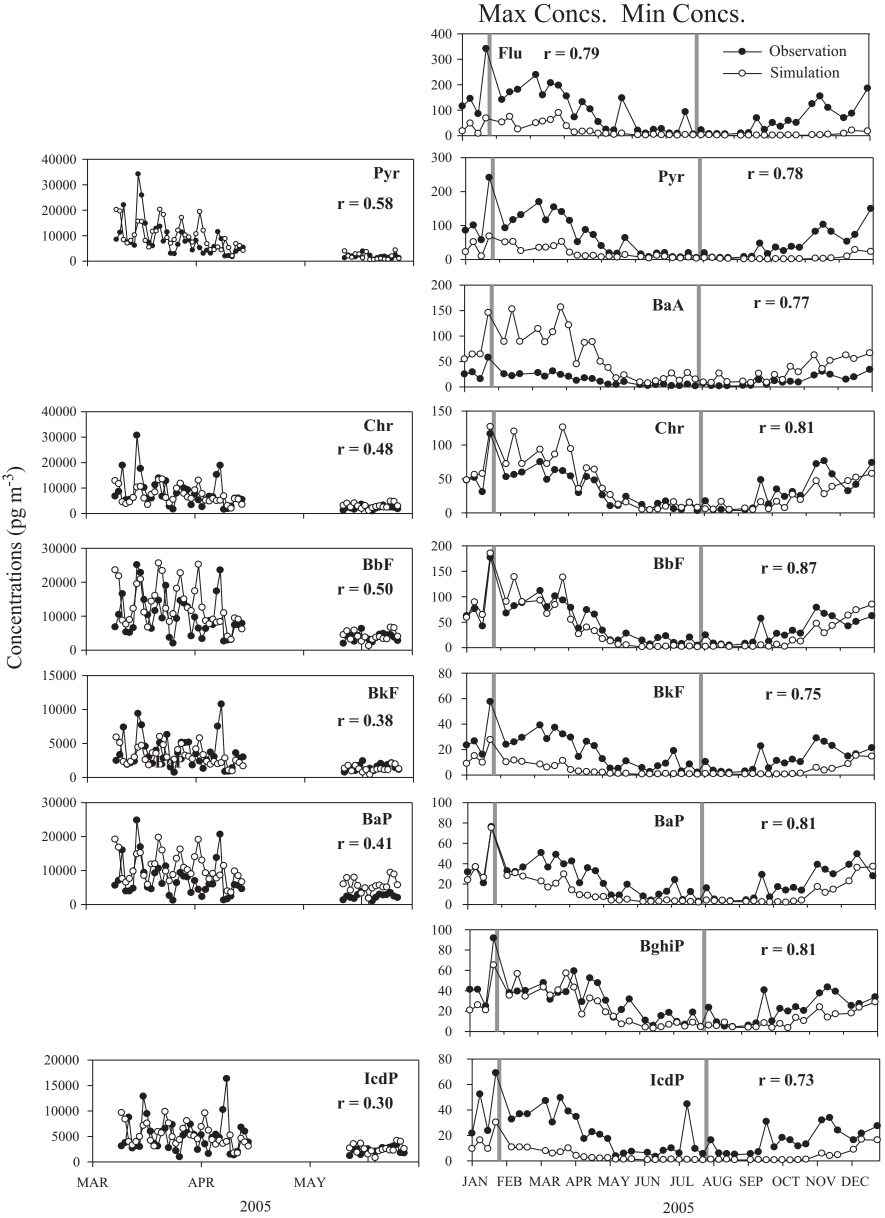

Fig. 13.4 Comparison of the measured and simulated concentrations of the particulate bound nine PAHs in Beijing (left panel) and Noto (right panel). The data in Beijing were a one-day average from March to May in 2005, whereas the Noto data were a weekly average from January to December in 2005. *r* is the correlation coefficient between the measured and simulated particulate concentrations. The vertical bars indicate the periods at which the maximum and minimum concentrations were observed

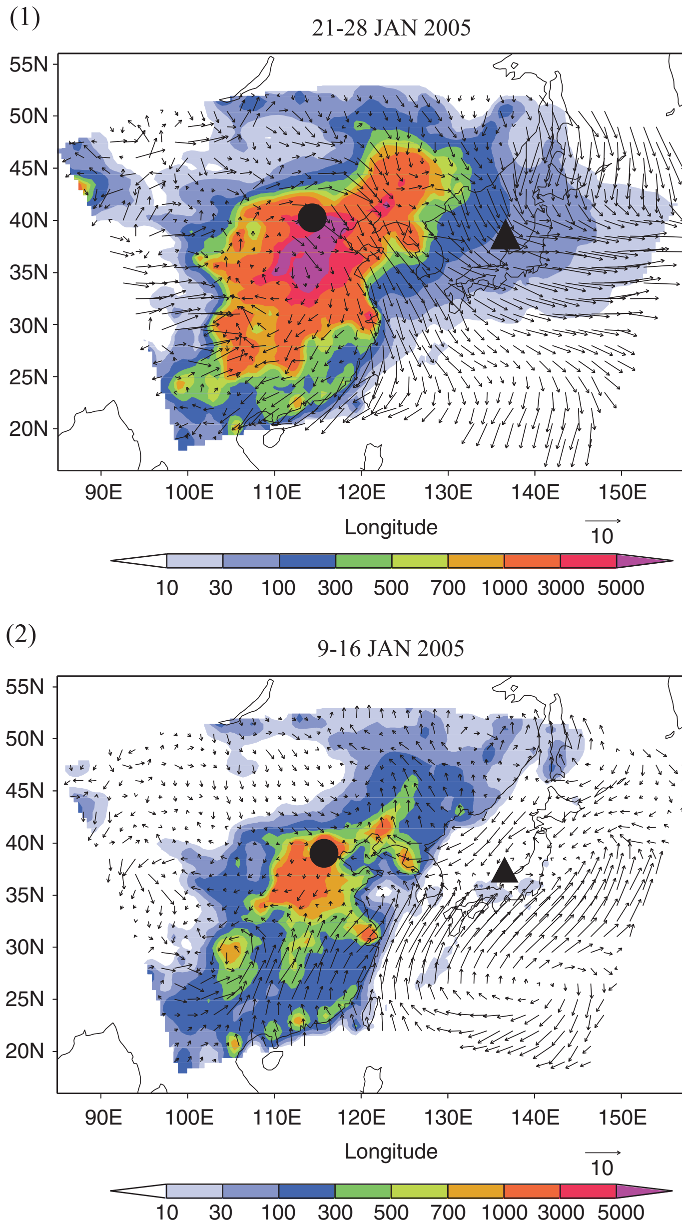

Fig. 13.5 Spatial distributions of BaP concentrations from (1) 21–28 January 2005 and (2) 9–16 July 2005. The scale is in units of pg m^{-3}. ● indicates the location of Beijing, and ▲ indicates the location of Noto. Arrow means the wind vector and speed (10 m sec^{-1})

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Part V

Polycyclic Aromatic Hydrocarbons in the Marine Environment

Chapter 14
PAHs in the Northwestern Japan Sea

T. Chizhova, Yu. Koudryashova, P. Tishchenko, and V. Lobanov

Abstract This chapter discusses the level of PAH pollution in the surface and deep waters of the northwestern part of the Japan Sea (NWJS). The investigated area included the river estuaries of the NWJS basin, the coastal regions, and the pelagic zone of the Japan Sea. As to spatial distributions, the concentration of 13 total PAHs ranged from 6.5 to 66.5 ng/L for river estuaries of South Primorye, and the concentration of 8 total PAHs was 31.2–105 ng/L for the Amur River Estuary. In the bays, the PAH content was 8–148.7 ng/L. The PAH pollution directly correlated with anthropogenic loads on surrounding territories. The open part of the Japan Sea demonstrates that the particulate PAH concentrations varied from 1.2 to 4.4 ng/L in 2009. There was an increasing trend for PAH content from the northeast of the Japan Sea to the southwest. Additionally, PAHs from coal and wood combustion predominated in surface waters of the north of the Japan Sea, while the main source of PAHs in the southwest of the Japan Sea was oil product combustion. In 2010 total PAH content ranged from 7.4 to 10.2 ng/L. The seasonal variation in the PAH concentrations was associated with emissions from the central and domestic heating systems. The results of the PAH distributions in the water column show that surface and intermediate waters (0–500 m) were more polluted than deep waters. Observed enhanced PAH levels on the depths from 30 to 500 m corresponded to biological pump activity.

Keywords Dissolved and Particulate Phase PAHs · Water Column PAH Distribution · The Japan Sea

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14.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) enter marine environments mainly through atmospheric particulate matter and precipitation and directly through air-water exchange or from river flows. Contamination from the latter is more typical of coastal waters, while the atmosphere is the main PAH source for the open sea. Direct PAH input due to oil spills during transportation or fuel spillage from vessels can occur as well. Therefore, surface waters are the main "gate" for PAH input into the sea and the oceanic water column.

In surface water, PAH composition profiles will change, depending on the physical and chemical properties of the environmental conditions (temperature, solar radiation, and others) (Tenhulscher et al. 1992; Bamford et al. 1999; Swietlik et al. 2002). It has been shown that low-molecular-weight (LMW) PAHs predominately dissolve in water, while high-molecular-weight (HMW) PAHs are associated with suspended matter (Schwarzenbach et al. 1993). Some studies propose that dissolved PAHs have greater bioavailability, and therefore, it is most essential to consider their levels in toxicity assessments (Webster et al. 2008). The compounds associated with suspended matter are transferred to deep-water zones as the suspended material settles and can then accumulate in the bottom sediments (Gustafsson et al. 1997 and references therein).

The Japan Sea contributes to the economy and ecology of Russia and other countries surrounding the sea. It is a marginal sea connected to others by shallow-water straits (not exceeding 150 m): through the Korea Strait to the East China Sea, through the La Perouse Strait and the Strait of Tartary to the Sea of Okhotsk, and through the Tsugaru Strait to the Pacific Ocean (Fig. 14.1). The Japan Sea is situated within two climatic zones, the northwestern zone (NWJS) with subarctic waters and the southeastern zone with subtropical waters (Leonov 1960). The Russian coastline extends for approximately 2100 km and belongs to several constituent entities of Russia. The population along this part of the Japan Sea numbers 1.44 million people (POMRAC, NOWPAP, UNEP 2007), making the NWJS coast in the Primorsky Krai (Primorye) region the most densely populated area, resulting in a higher anthropogenic impact. In addition, the transboundary transfer of pollutants through the atmosphere reinforces the influence on the environment in the region (Tamamura et al. 2007). The NWJS is also polluted by petroleum discharge from vessels because of the intense coastal and international shipping activities. Continuous industrial development in the northern China regions and the eastern regions of Russia may result in increasing input of pollutants, including PAHs. However, there have not been significant recent studies on PAHs in the Russian part of the Japan Sea.

This chapter is concerned with the spatial and temporal distribution of PAHs in the waters of the Russian Far East, more specifically, in the northwestern part of the Japan Sea in its coastal and deep-sea regions, as well as in the Amur River Estuary and rivers of the NWJS basin.

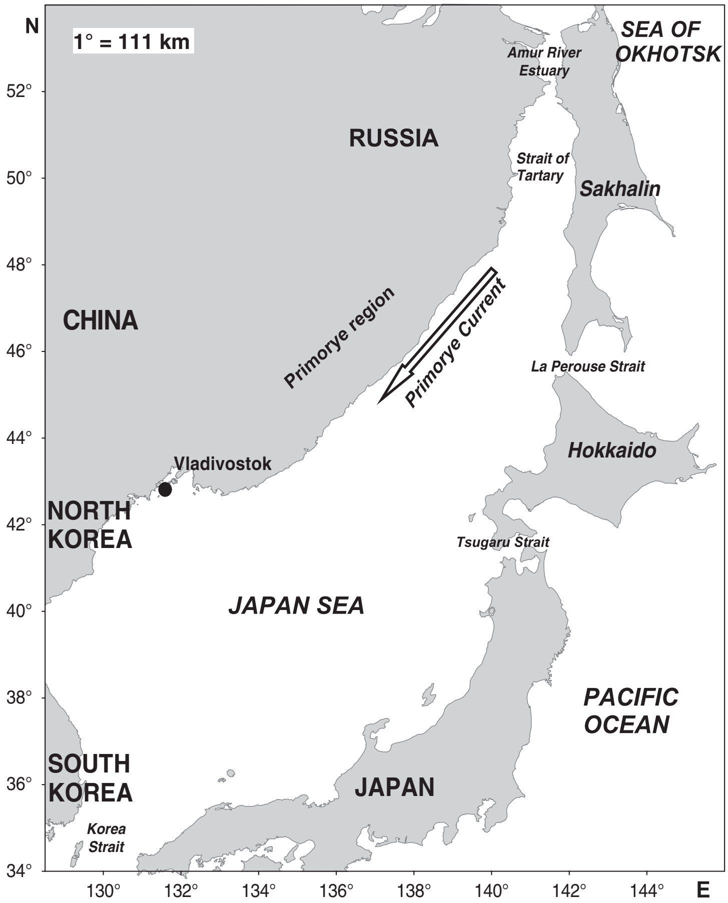

Fig. 14.1 A map of the Japan Sea

14.2 PAHs in the Surface Waters

14.2.1 PAHs in the Rivers

Few rivers flow into the Japan Sea from mainland Asia; the largest rivers of the NWJS basin are the Tumen River, the Tumnin River, the Razdolnaya River, and the Partizanskaya River. The three latter rivers flow through the Primorsky Krai territory (Fig. 14.2a). The Tumnin River flows through unpolluted areas into the Tatar Strait. At present, there is no information on PAH content in it. The Amur River may also influence the NWJS; in winter, the flow from the Amur River Estuary is found to lead directly to the northern part of the Japan Sea (Zhabin et al. 2009) from where

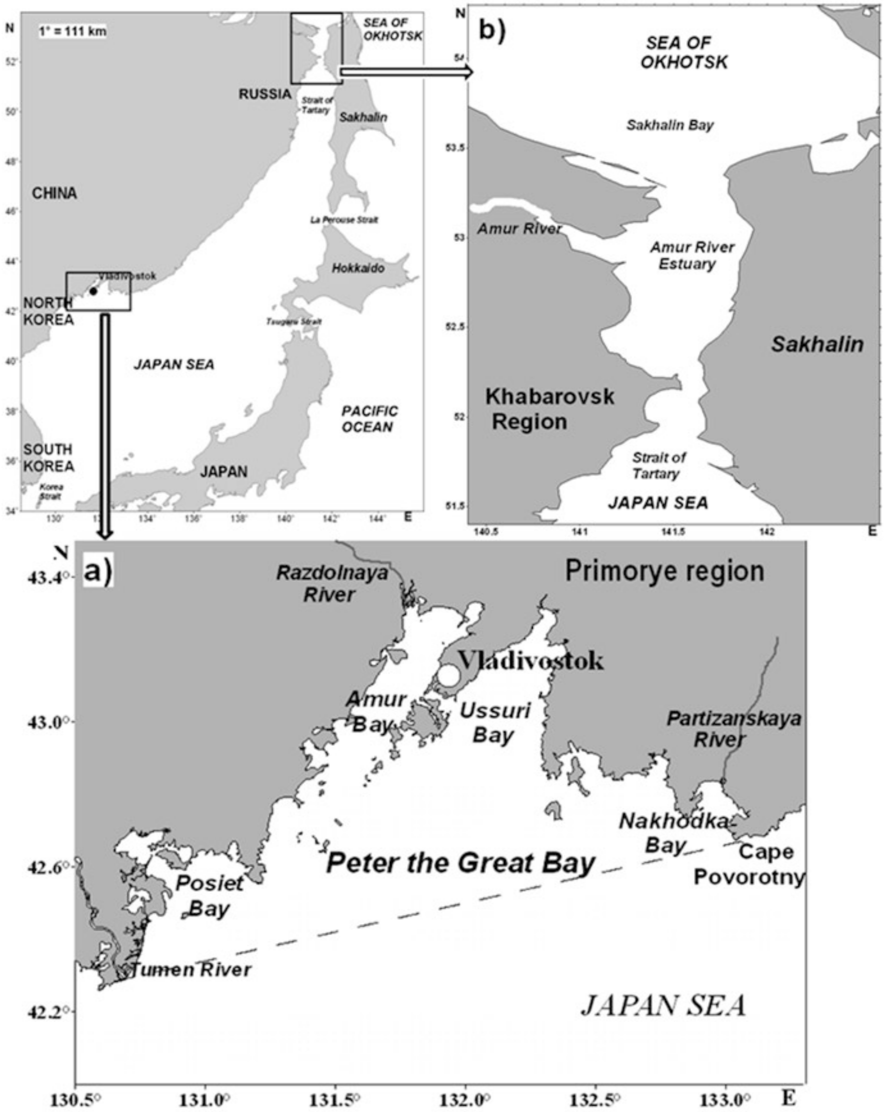

Fig. 14.2 The PAH study locations are in the NWJS coastal waters: (**a**) the Peter the Great Bay; (**b**) the Amur River Estuary

the Amur River's waters enter the NWJS from the Primorye Current (Figs. 14.1 and 14.2b). It should be noted that the Tumen River, the Amur River, and rivers in the southern regions of Primorye running through areas with intensive anthropogenic activities are contaminated by different pollutants, including PAHs.

The Tumen River, the Amur River and its estuary, and the Partizanskaya River Estuary have been the most investigated for PAH contamination.

The Tumen River running into the NWJS south of the Posiet Bay flows over the southeast Jilin Province in Northeast China (Fig. 14.2a). The length of the river is 525 km, from which 510 km form the border between China and North Korea. The Tumen River is an important water resource used by both countries for domestic, agricultural, and industrial needs.

The following total concentrations of 15 dissolved PAHs (DPAHs) and PAHs sorbed onto suspended particulate matter (PPAHs) in the surface waters of the Tumen River were found by Chinese authors (Cong et al. 2010; Jin et al. 2012): 27–1050 and 37–820 ngL^{-1}, respectively. It was shown that the highest concentrations of DPAHs and PPAHs were observed in spring. The same studies showed that the dissolved phase (DP) contained the highest concentration of Phe, Fle, Pyr, and Flu, while the particulate phase (PP) was characterized by the highest concentrations of Phe, Flu, Pyr, and Fle. The contents of LMW (three-ring) PAHs in DP and in PP were 74% and 52%, respectively. Research shows that the ice covering the river in the winter accumulates PAHs; therefore the highest concentration of PAHs in March is caused by the ice melting.

Calculations of the PAH diagnostic ratios Ant/(Ant + Phe) and Flu/(Flu + Pyr) allow confirmation that combustion processes are the main sources of PAH pollutants in the Tumen River's waters regardless of the season. According to different studies, industrial development in the northeastern regions of China and North Korea continuing from the 1960s has increased the input of pollutants into the Tumen River basin (Cong et al. 2010; Nigmatulina and Chernyaev 2015). The chemical, cellulose, and metallurgical industries of the People's Republic of China and the DPRK are the main sources of pollutants in the region (Cong et al. 2010). In addition, the annual population growth of 25% in the Jilin Province of China (Nigmatulina and Chernyaev 2015) causes increased pollution of the river due to domestic emissions (heating, motor transport, and others).

The Amur River is one of the world's largest rivers. The Amur River basin is situated in the Far East within the boundaries of three countries: Russia, China, and Mongolia. The Amur River is an important traffic artery with a navigable waterway length of up to 1550 km. Approximately 75 million people live in the river basin, using its waters for industrial, agricultural, and domestic needs and is thus a source of pollution. Despite this, there have not been a significant number of publications devoted to studying PAH pollution in the Amur River. The only reports examine the PAH concentration in the middle Amur River waters (Khabarovsk city region) in 2001–2002 (Kondratjeva et al. 2007) and the distribution of PAHs in the Amur Estuary in 2006 (Chizhova et al. 2012, 2013c).

In the middle Amur River, the total concentration of 9 PAHs (9TPAH) in surface waters was found to be 3.05 ngL^{-1} in November 2001 and 9.8 ngL^{-1} in January 2002, with predominant compounds of Pyr, Ant, and BgPe (Kondratjeva et al. 2007). The authors suppose that PAH pollution of the Amur River is caused by anthropogenic factors, such as the building of water storage basins, transport pollution, fuel combustion, input of contaminants from overland flow, and forest fires, among others.

In June 2006, a study of the PAH concentrations in the Amur Estuary surface waters showed that total DPAH concentrations from the sampling stations varied from 25 to 91.4 ngL^{-1} (mean 46.6 ngL^{-1}); total PPAH concentrations varied from 6.2 to 13.6 ngL^{-1} (mean 9.9 ngL^{-1}), which is equivalent to 184–1388 ngg^{-1} (mean 668 ngg^{-1}) in terms of suspended matter units (Chizhova et al. 2012, 2013c). There were 12 PAHs determined in the samples with differing composition and are as follows: Nap, Ace, Fle, Phe, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, and BgPe in the DP and Nap, Fle, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, and BgPe in the PP. The study determined the predominance of two- and three-ring PAHs (81–97%) in the water, with the Nap concentration at most stations amounting to 43–79% of the total DPAH concentration, followed by the domination of Phe, Fle, Pyr, and Ace (in descending order of concentration). The concentration of two- to three-ring PPAHs reached 80–90% of the total PAH content. The studied area showed Phe as a predominant component of the PPAH concentration. Comparatively high concentrations of Nap, Fle, Pyr, and Flu (in descending order of concentration) were also recorded. The concentration of four- to six-ring PPAHs amounted to 10–20% of the total PPAH content.

Approximately 90% of suspended organic matter and 40% of dissolved organic matter are known to deposit in the rivers' estuarial areas where mixing of marine and river water occurs (Lisitsyn 1995). However, no relationship was found between the concentration of four- to six-ring DPAHs and the salinity in the Amur Estuary, while reduced two- to three-ring DPAH concentrations have been observed with an increase in salinity (Chizhova et al. 2013c). At the same time, the PPAH density was higher in the seaward estuarial part than in the riverward part, which showed high concentrations of suspended matter. Therefore, there was practically no relationship between the volume concentration of PAHs and the salinity due to input of PAHs into estuarial surface waters from the atmosphere. Reduced concentrations of LMW DPAHs with increasing salinity occur due to the greater destruction of PAHs in the atmosphere compared with that of HMW compounds (Cerniglia 1992).

The calculation of PAH isomer pair ratios showed that PAHs in the Amur Estuary came from combustion processes (ratio BaA/(BaA + Chr)), predominately petroleum combustion (ratio Flu/(Flu + Pyr)), while the ratio of Ant/(Ant + Phe) showed that petrogenic processes produced PAHs at all stations. In fact, PAHs of different origin can be expected in the Amur Estuary due to industrial processes (emissions of coal-burning boiler stations and the like, forest fires), land and water transport, and coal dust entering the Amur River estuarial waters from open coal-supply barges.

In several studies, we investigated the PAH distribution in the surface waters of *rivers in South Primorye running into the NWJS* (Koudryashova et al. 2012; Chizhova et al. 2013b; Koudryashova and Chizhova 2014).

Studies in June and July 2010 showed that concentrations of 13 TPAHs in the surface waters and the bottom sediments varied between 7.5–44 ngL^{-1} and 45.4–135.8 mgkg^{-1}, respectively (Koudryashova et al. 2012; Chizhova et al. 2013b). It was found that rivers flowing through environmentally unpolluted regions were characterized by low PAH concentrations in the water and bottom sediments, and

Table 14.1 Seasonal PAH concentrations (ngL^{-1}) in the Partizanskaya River surface water during 2012

	Winter	Spring	Summer	Autumn
TPAH	32–66.4	7.16–21.92	15.81–24.53	9.47–23.37
	(38.88)	(17.06)	(20.11)	(17.06)
DPAH	30.62–60.55	5.83–20.6	14.73–22.8	8.57–22.37
	(36.7)	(13.5)	(18.8)	(16.0)
PPAH	1.11–5.85	0.97–3.57	1.04–1.72	0.71–1.25
	(2.1)	(1.59)	(1.34)	(1.01)

Mean PAH concentrations in ng/L are in parantheses

otherwise, high PAH concentrations have been observed in the water and bottom sediments in areas with high industrial activity.

The Partizanskaya River, being one of the largest rivers in South Primorye (Pavlova et al. 2015) and running into the Nakhodka Bay, has been studied in more detail (Fig. 14.2a). Pollution of the river estuary is mostly caused by discharge from industrial enterprises and seaports located in Nakhodka City and the Nakhodka Bay. In winter, during the heating season, the combustion of coal and wood is added to the permanent sources of pollution.

Seasonal variations in the DPAH and PPAH concentrations in the surface waters of the Partizanskaya River are presented in Table 14.1. It should be noted that the maximum PAH concentration in the river was observed in the winter and resulted from higher anthropogenic impact due to additional seasonal sources of pollution, such as emissions from heat boiler stations and domestic wood and coal combustion (Koudryashova and Chizhova 2014). Fle, Ace, and Pyr dominated the DPAH composition in winter and autumn and Ace, Fle, and Pyr in spring and in summer, while in the PPAH profile, Pyr, Fle, and Chr were prevalent in winter and Pyr, Flu, Fle in the other seasons.

Calculation of the PAH isomer ratios Flu/(Flu + Pyr), BaA/(BaA + Chr), and IDP/(IDP + BgPe) showed that PAHs in the Partizanskaya River in winter came from petroleum combustion (50% of the total source), coal combustion, and petrogenic sources (31%). Koudryashova and Chizhova (2014) found that the concentration of PAHs in the ice layer was higher than those in the water under the ice. During sampling, an abundance of coal dust was registered at the surface of the river's ice sheet. Apparently, emissions from heat boiler stations and domestic heating allow PAHs originating from coal combustion to enter the estuarial zone. In spring and summer, PAHs originated from petrogenic and petroleum combustion processes with the latter the predominant source. The presence of petroleum combustion-generated PAHs over the year is generated by the numerous industrial and transport activities within the surrounding estuary grounds; petrogenic PAHs enter the river with coal dust from the coal terminals in Nakhodka Port.

Comparing individual PAH concentrations in the rivers and estuaries with those in the global environmental media (Wang et al. 2013), we note that concentrations of different DPAHs and PPAHs in the Tumen River were relatively high on a

Table 14.2 Reported PAH concentrations in the estuarine waters of East Asia

Research area	Year	N	DPAH, ngL^{-1}	PPAH, ngL^{-1} or ngg^{-1}*	Predominant PAH	References
Pearl Estuary, China	2001	16	1306–6050	150.3–289.8	98.2–98.6% Nap in DP	Luo et al. (2004, 2006)
				422–1850*	Fle, Phe, Nap in PP	
Daliao Estuary, China	2005	18	1333	3642*	3-ring PAHs	Guo et al. (2007)
Yangtze Estuary, China	2006	–	478–6273[a]		–	Ou et al. (2009)
Yellow River Delta	2007	16	64.8–334.6	65.6–675.4*	2-3-ring PAHs	Wang et al. (2009)
Yangtze Estuary, China	2010	16	12.9–638.1[a]		Flu, Nap, Pyr, Phe	Zhang et al. (2012)
Amur Estuary, Russia	2006	12	25–91.4	6.2–13.6	DP: Nap, Phe, Fle, Pyr, Ace	Chizhova et al. (2012, 2013c)
				184–1388*	PP: Phe, Nap, Fle, Pyr, Flu	
Partizanskaya Estuary, Russia	2012	13	5.8–60.6	0.71–5.85	See above	Koudryashova and Chizhova (2014)

N- a number of investigated PAHs

[a] TPAH concentration (DPAH+PPAH), ngL^{-1}. It should be noted that the pretreatment method used for PP was different: pretreatment for the samples from the Japan Sea collected in 2011, the Partizanskaya River, the Nakhodka Bay, and the Posiet Bay was the same as that described in Chizhova et al. (2013a), but pretreatment of the samples from the Amur River and the Japan Sea collected in 2009-2010 includes liquid-liquid extraction (LLE) before additional cleanup with Silica cartridges. In our opinion, the use of LLE provides a more complete extraction

*means ngg^{-1}

worldwide scale, while DPAH and PPAH concentrations in the Amur River and its estuary as well as in the Partizanskaya Estuary were below average and low.

Table 14.2 shows recent data comparing PAH concentrations in the river estuaries of the NWJS basin and in the East Asia region. PAH concentrations in the river estuaries of the NWJS basin were lower than those in the rivers of the East Asia region, which corresponds to lower anthropogenic impact in the NWJS basin. However, the method of PAH sample preparation used by the researchers must be considered, as differences in methods can result in a large spread in the data. In addition, differences in the composition of the compounds being studied must be considered, for example, the total concentration of 15 DPAHs in the Pearl Estuary ranged only from 19.5 to 90.5 ngL^{-1} after subtracting the concentration of Nap (Table 14.2) (Luo et al. 2004, 2006).

Results of these studies have shown that PAH contamination of the studied rivers is highly correlated with the intensity of anthropogenic impact to the territory adjacent to the river. Atmospheric input of PAHs into the estuarial zones has been proven. The cold period is characterized by higher concentrations of PAHs in the river and estuarial waters due to emissions from central and domestic heating. Considering the low PAH concentrations in the estuarial surface waters in the Russian part of the NWJS, it is expected that the amount of pollutants entering the NWJS with the river flow is also not large.

14.2.2 PAHs in the Marine Coastal Zones

The Japan Sea, especially the northern part, has a few bays and gulfs, including the Peter the Great Bay, the Olga Bay, and the Ishikari Bay. The Peter the Great Bay is the largest bay in the NWJS. Its sea line extends northeast from the mouth of the Tumen River to Cape Povorotny (Fig. 14.3). The indented bay coastline forms many smaller bays, such as the Amur Bay, the Posiet Bay, the Ussuri Bay, and the Nakhodka Bay, among others (Fig. 14.3). Economic upturn in Russia in the 2000s led to the activation of industrial production and an increased rate of growth in territories adjacent to the Peter the Great Bay (Khristoforova et al. 2015). In addition, at present, more than 80% of the population is concentrated in these areas, resulting in greater volumes of sewage and emissions. Because of this, the bay is exposed to anthropogenic influence, the most among the Russian water areas of the NWJS (Naumov 2006). Different contributions from the interior bays to pollution of the Peter the Great Bay depend on the volume of industrial and domestic discharge from the coastal areas (Chernyaev and Nigmatulina 2013). In this part of the

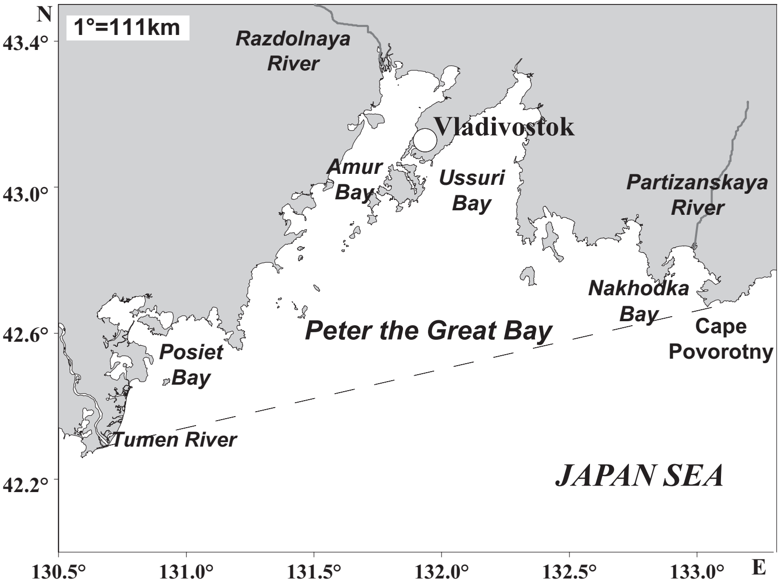

Fig. 14.3 A map of the Peter the Great Bay

Table 14.3 Reported PAH concentrations in the dissolved and particulate phases and sediments (SPAH) in the bays of NWJS

Research area	Year	N	DPAH, ngL^{-1}	PPAH, ngL^{-1} or ngg^{-1}*	SPAH, ngg^{-1}*	Predominant PAHs	References
Amur Bay, southwestern part	2005/April	10	3.54–17.47[a]		7–1100	Water: Perylene, Flu	Nemirovskaya (2007)
Amur Bay, eastern part	2015/June	13	17.55–148.69[a] (mean 47.48)		–	Fle, BaP, BgPe, Ace, BbF	Unpublished data
Nakhodka Bay	2011/Nov.	13	40–72	0.52–1.36	–	DP - Fle, Pyr, Ace, Flu; PP – Fle, Pyr, Flu	Unpublished data
	2012/April		8.1–28.9	0.69–4.1			Unpublished data
Nakhodka Bay	2013/Aug.	15	–		1.76–68.12	Phe, BbF, Fle, Flu	Zhuravel et al. (2015)
Possyet Bay	2013	13	8–29[a]		–	DP – Ace, Pyr, Fle; PP – Flu, Pyr	Koudryashova and Chizhova (2016)

[a]TPAH concentration (DPAH+PPAH), ngL^{-1}

*means ngg^{-1}

chapter, we will consider PAH pollution in the Amur Bay, the Nakhodka Bay, and the Posiet Bay, as the most investigated interior bays.

Studies of the southwestern part of *the Amur Bay* in April 2005 showed concentrations of ten TPAH in the surface waters in the range of 3.54–17.47 ngL^{-1} (Table 14.3), with a predominance of perylene and Flu, the concentrations of which were more than 60% in the water samples (Nemirovskaya 2007). In the surface layer of the bottom sediments, the concentrations of ten TPAH varied between 7 and 1100 ngg^{-1}. Flu, Pyr, and Ant displayed the highest concentrations. Calculation of the isomer ratios showed that PAHs in the water and in the bottom sediments had petroleum and a pyrogenic origin, i.e., they came from anthropogenic sources (Nemirovskaya et al. 2006).

Samples taken along the coast in the eastern part of the Amur Bay in the summer of 2015 showed higher total concentrations of 13 TPAHs in the surface water compared with that in the southwestern part, which ranged from 17.55 to 148.69 ngL^{-1} (mean 47.48 ngL^{-1}), with a dominance of Fle, BaP, BgPe, Ace, and BbF (Table 14.3). It should be noted that the BaP concentration of 5 ngL^{-1} exceeded values permitted in the aquatic environment by the Russian Federation (Bespamyatnov and Krotov 1985). High concentrations of five- to six-ring PAHs indicated that PAHs entered into the eastern part of the bay from anthropogenic sources, while high BgPe and BbF concentrations in the waters are indicative of PAHs associated with gasoline engine exhaust (Lima et al. 2005).

When analyzing results obtained in the Amur Bay, higher PAH concentrations observed in the eastern part were caused by the following factors:

1. Vladivostok, the largest city and port in the Russian Far East– an agglomeration with a population of more than a million – located at the bay on the eastern coast, permits residential and industrial waste waters to enter this part of the bay (Chernova et al. 2011).
2. A large oil fuel terminal for bunkering is situated here.
3. Investigation of the southwestern part of the bay conducted in 2005 showed that the economic crisis of the 1990s, which caused a decline in manufacturing output, resulted in reductions in pollutants entering the environment, whereas the eastern Amur Bay waters studied during a 10-year surge in the economy showed increased pollutant volume, including PAHs, which reached the environment.

Studies in *the Nakhodka Bay* showed that the total concentration of 13 DPAHs in the surface waters varied between 41.1 and 78.2 ngL^{-1} (mean 58.9 ngL^{-1}) in late November 2011 and was significantly lower (from 8.1 to 28.9 ngL^{-1} with mean of 14.4 ngL^{-1}) in April 2012 (Table 14.3). In autumn and spring, the concentration of 13 PPAHs varied between 0.96–1.56 ngL^{-1} (mean 1.14 ngL^{-1}) and 0.69–4.1 ngL^{-1} (mean 2.17 ngL^{-1}), respectively. It should be noted that in spring and autumn, the PPAH concentration had a direct relationship with the amount of solids, which was 25% higher in spring than in autumn. In autumn and spring, Fle (46%), Pyr (24%), Ace (11%), and Flu (9%), and Ace (48%), Fle (22%), Pyr (15%), and Flu (13%) were dominant in DP, respectively; the main PAH component in PP was Fle (35%), Pyr (13%), and Flu (11%) in November and Pyr (33%), Flu (31%), Chr (9%), and BgPe (7%) in April.

In autumn, the PAH sources calculated from the diagnostic ratios Flu/(Flu + Pyr), BaA/(BaA + Chr), and IDP/(IDP + BgPe) were both pyrogenic (petroleum combustion) and petrogenic, while in spring, PAHs originated from the incomplete combustion of petroleum and its derivatives (ratios Flu/(Flu + Pyr), IDP/(IDP + BgPe)). Data obtained from calculation of the ratios agree with differences in DPAH and PPAH composition in the studied seasons. For example, in spring, the ratios showed PAHs originating from the incomplete combustion of petroleum, with Ace predominating in the DPAHs, and BgPe generated by gasoline combustion (Lima et al. 2005), which was predominant in the PPAHs. In autumn, the predominance of Fle in both phases can be associated with petrogenic sources of PAHs in the bay waters (Achten and Hofmann 2009; Abrajano et al. 2014).

For the bottom sediments in the Nakhodka Bay, there are different data for the total concentration of PAHs in different parts of the water area. Studies in 2008 registered a variation in TPAHs between 0.3 and 168.3 ngg^{-1} (Grigoryeva and Pitruk 2010), while the concentrations of 15 TPAHs in August 2013 ranged from 1.7 to 68.12 ngg^{-1} (Zhuravel et al. 2015). The predominant components found in the second study were Phe, BbF, Fle, and Flu. The authors showed the bottom sediments were of pyrogenic and petrogenic origins; the petrogenic source was coal dust found in the bottom sediments, which entered from the bay coal piers during open coal handling.

When discussing these findings, it should be stressed that the Nakhodka Bay is one of the most developed water areas in Primorye. Nakhodka City and Port, Vostochny Port coal terminals, oil terminal Kozmino, and others located on the coast contribute to the PAH pollution in the Nakhodka Bay (Nigmatulina et al. 2011; Khristoforova et al. 2015). At the beginning of the heating season in late October, emissions from the heating plants add pollutants to these permanent PAH sources in the bay, which shows isomer ratios characteristic of coal and wood combustion and results in a high PAH concentration in the bay waters. The presence of petrogenically generated PAHs can be attributed to both petroleum micro-spills from vessel fuel tanks and the entry of coal dust into the bay waters from the port terminals. The latter has been shown for the Partizanskaya Estuary adjacent to the Nakhodka Bay in the *River Input* chapter hereof. Furthermore, coal dust particles were found in the Nakhodka Bay sediments (Zhuravel et al. 2015).

In *the Posiet Bay*, PAH concentrations ranged between 8 and 29 ngL^{-1} during 2013 (Table 14.3). The highest concentrations were detected for Ace, Pyr, and Fle in water and Flu and Pyr in suspended matter (Koudryashova and Chizhova 2016). It may be noted that the Posiet Bay waters are the least polluted in comparison with the Nakhodka Bay and the Amur Bay, which correlates with the lowest volumes of industrial and domestic discharge.

The findings show that PAH pollution levels decrease in the order of the Nakhodka Bay, the Amur Bay, and the Posiet Bay. This distribution, to some extent, does not agree with data for the input of pollutants from domestic and industrial plant effluents, representing intense anthropogenic activity, which according to expert assessments are 2.23 gm^{-3} for the Amur Bay, 0.83 gm^{-3} for the Nakhodka Bay, and 0.081 gm^{-3} for the Posiet Bay (Nigmatulina and Chernyaev 2015). However, seasonal variations in the PAH concentrations in the surface waters of these bays should also be considered. The Amur Bay was studied in the summer, and thus we obtained minimal PAH concentrations in the water in comparison with the other seasons due to the lack of influence by domestic and central heating. In addition, one can see that in spring, the TPAH concentration in the Nakhodka Bay (mean 16.6 ngL^{-1}) correlates with the mean TPAH concentration in the Partizanskaya River (17 ngL^{-1}). Considering the same pollution sources are present for the estuarial and sea waters, we can expect that summer PAH concentrations in the Nakhodka Bay will also slightly differ from that in the Partizanskaya Estuary (Table 14.1). At the same time, summer data for the Amur Bay, ranging from 17.55 to 148.69 ngL^{-1} (mean 47.48 ngL^{-1}), are notably higher. Thus, with reference to the pollutants entering the bays (Nigmatulina and Chernyaev 2015), we suggest that the Amur Bay is the most polluted with PAHs. This conclusion is also confirmed by higher PAH concentrations in the Amur Bay sediments (Table 14.3) obtained in the beginning of the region's economic advance in comparison with those in the Nakhodka Bay's bottom sediments in 2013 (Nemirovskaya 2007; Zhuravel et al. 2015). However, it should be noted that the bottom sediments from the Nakhodka Bay were mostly composed of gravel and sand, which has a lower sorption ability for PAHs (Budzinski et al. 1997).

The presented data suggest that the levels of PAH contamination in the coastal zone have been growing in the past decade due to industrial development of the region. As a whole, the distribution of pollutants along the coast of the Japan Sea is characterized by irregularity and depends on the anthropogenic load intensity of the territory.

14.2.3 PAHs in the Pelagic Zone

PAH pollution studies of the Japan Sea surface waters were conducted in July 2009 and August 2010 during two cruises (Chizhova et al. 2013a, 2015).

In July 2009, the total concentration of 13 PPAHs ranged from 1.2 to 4.4 ngL^{-1} with a mean of 2.7 ngL^{-1}, which based on the suspended matter unit mass, was 193–2447 ngg^{-1} with mean of 806 ngg^{-1} (Chizhova et al. 2015). There was a difference between the PPAH distribution in the western and northeastern waters of the sea (Figs. 14.4 and 14.5). The western part was characterized by higher PPAH concentrations and a more even distribution, ranging between 3 and 4.4 ngL^{-1} with a mean of 3.6 ngL^{-1}. In the northeastern part, the PPAH concentration varied from 1.2 to 3.5 ngL^{-1} (mean – 2.2 ngL^{-1}). In the north, higher concentrations of PPAHs were observed at stations located close to the Primorye territory (st. 13, 14, 17) and the Sakhalin and Hokkaido islands (st. 20, 21). It was found that Ace, Pyr, Fle, and Flu had the highest concentration in both parts of the sea. The content of these compounds was 18–42% (mean 27%) for Ace, 6–29% (mean 21%) for Pyr, 11–22% (mean 16%) for Fle, and 4–19% (mean 10%) for Flu. In general, three-, four-,

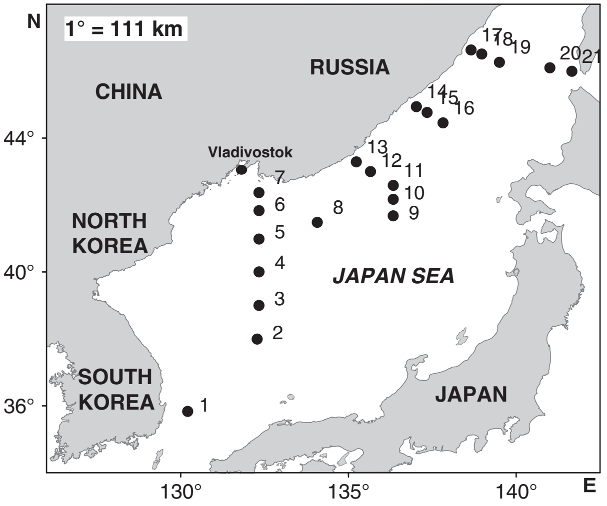

Fig. 14.4 Locations of the sampling sites in July 2009

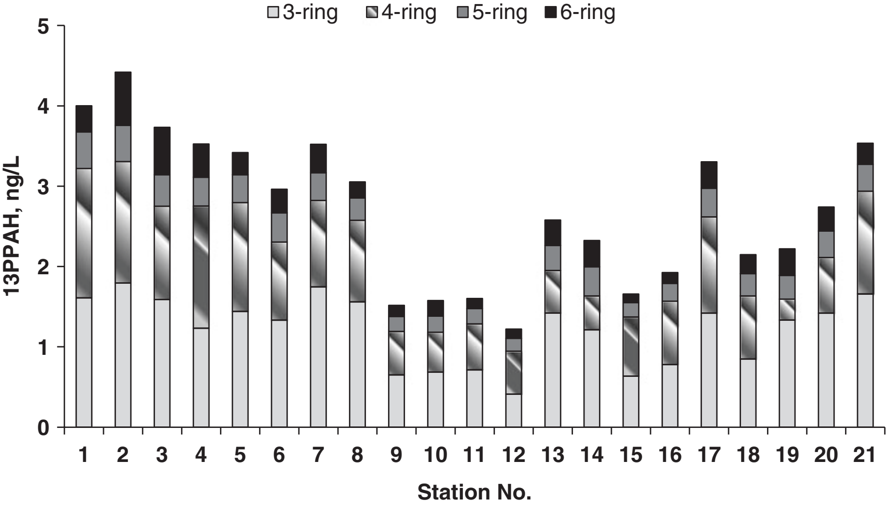

Fig. 14.5 PPAH concentrations and composition profiles at the stations in the NWJS in July 2009

five-, and six-ring PPAHs account for 44.7%, 33.4%, 11.5%, and 10.4% of total PPAHs, respectively.

Such a distribution of PAHs can be attributed to varying levels of anthropogenic influence on the studied water areas. Thus, high PAH concentrations in the western part of the sea are caused by pollutant ingress from surrounding industrialized and developing areas (Japan, South Korea, DPRK, north regions of China, and the southern region of Primorsky Krai, Russia). The lower PAH concentrations found in the northeastern sea areas can be attributed to the low industrialization of the surrounding territories. As known, there are no large industrial centers in the northern regions of Primorsky Krai, the eastern part of Khabarovsk Krai, or Sakhalin Island surrounding this region of the Japan Sea.

As the open area of the Japan Sea is situated at a distance from the coastal sources of PAHs and the atmosphere is the main source of PAHs, air circulation over the sea (winds) should be considered. Figure 14.6 presents a wind vector diagram over the Japan Sea surface showing the prevalence of winds from the south over the western part of the sea. As it follows from this diagram (Fig. 14.5), surface waters in the western part contained higher concentrations of PPAHs than those in the northeastern part, with a gradual decline from south to north. Therefore, it can be assumed that PAHs enter this part of the sea mostly from atmospheric transfer from the southern territories (Japan, South Korea, and southern regions of China). In summer, there are no obvious prevailing winds above the central part of the sea, and thus PAHs originate from anthropogenic sources from different territories, resulting in lower PAH concentrations in the waters (Figs. 14.5 and 14.6). In the north area of the sea (between the mainland and Sakhalin Island), the wind vector increases again, and thus it is reasonable to expect an input of PAH pollutants to this part of

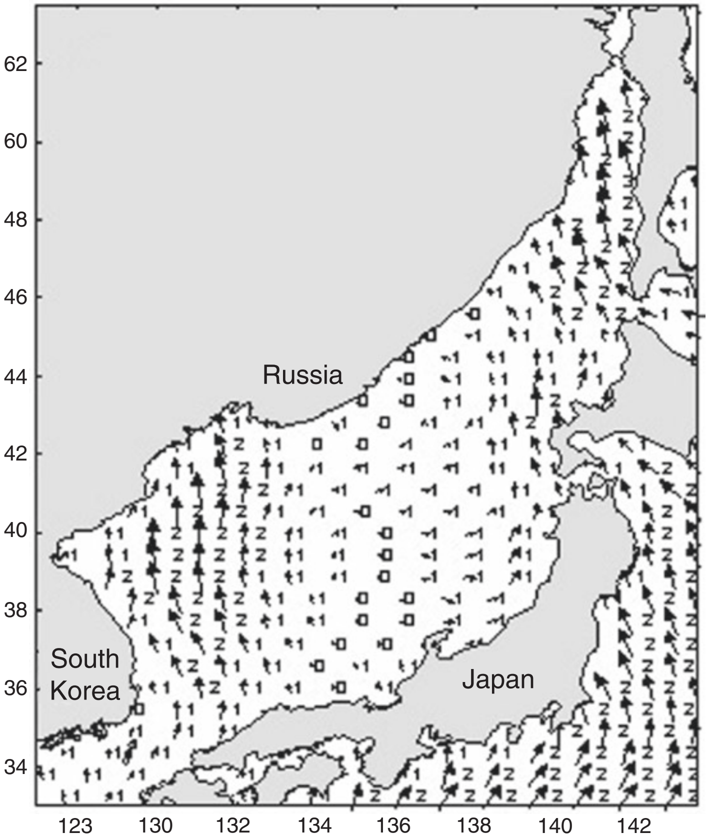

Fig. 14.6 Summer mean wind vector over the Japan Sea in 1991–1998 (http://rus.ferhri.ru/japan/Meteo/Meteo_wind_direct.htm)

the sea from the Sakhalin and Hokkaido islands and a higher concentration of PAHs at stations 20 and 21 (Fig. 14.5) associated with that.

Since shelf zones that are part of the sea area adjacent to continents have a wide species diversity and are regions for harvesting aquatic bioresources (Doronin 2007), the pollution dynamics there should be controlled. As previously mentioned, the western part of the sea contained relatively uniform PAH concentrations, and there was no difference in PAH concentration between shelf station 7 and the offshore stations. However, we had some shelf sampling stations (13, 14, 17, 20, and 21) in the northeastern part of the sea. The mean concentration of PPAHs found (3.1 ngL^{-1}) was 48% more than that in the deep-sea zone (1.6 ngL^{-1}). These results are consistent with an increase in pollution depending on the proximity to PAH sources, which are located along the coastal area.

During the cruise in August 2010 (Fig. 14.7), TPAH concentrations varied from 7.4 to 10.2 ngL^{-1} with a mean of 8.5 ngL^{-1} (Chizhova et al. 2013a). Concentrations

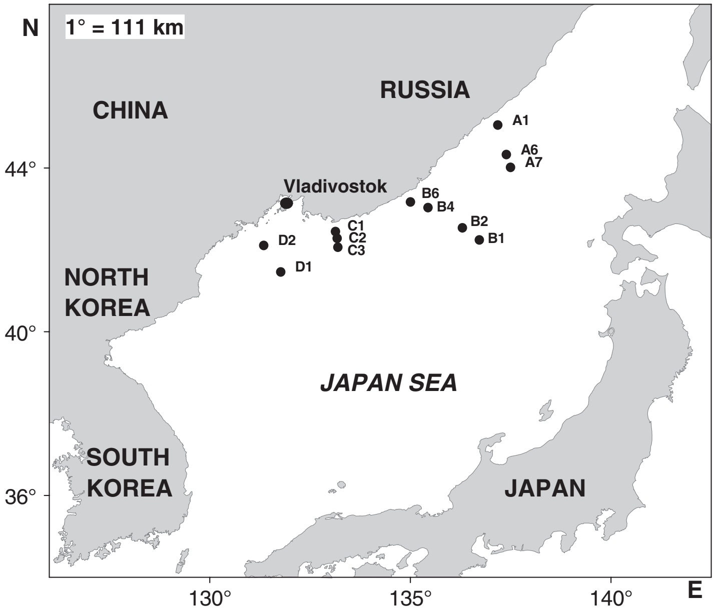

Fig. 14.7 Location of the sampling sites in August 2010

of DPAHs and PPAHs ranged between 4.8–6.5 ngL^{-1} (mean 5.6 ngL^{-1}) and 2.1–3.7 ngL^{-1} (mean 2.7 ngL^{-1}), respectively. PAH concentrations normalized to the suspended matter varied between 454 and 2418 ngg^{-1} with a mean of 1257 ngg^{-1}. A study of the composition showed the dominance of three- to four-ring DPAHs and PPAHs, namely, Fle (33–42%, mean 38%), Pyr (16–36%, mean 23%), Ace (15–17%, mean 16%), Flu (4–14%, mean 11%), and Ace (19–35%, mean 26%), Pyr (8–36%, mean 21%), Fle (13–19%, mean 16%), and Flu (6–23%, mean 11%), respectively. Three-, four-, five-, and six-ring compounds in the water and the suspended matter constituted 60.3%, 36.4%, 2%, and 1.3% and 43.9%, 37.6%, 9.5%, and 9%, respectively. The concentrations of three- to four-ring DPAHs (excluding Chr) were higher than the concentrations of PPAHs. However, Chr and five- to six-ring PAHs were two to five times higher in the suspended matter than in the water. In the Amur Estuary, we found the same proportion (Chizhova et al. 2013c). Gustafson and Dickhut (1997) showed a similar distribution between water and suspended matter for both a relatively uncontaminated site and a contaminated site in the southern Chesapeake Bay, Virginia, USA. Thus, it can be assumed that similar PAH proportions in the large water bodies result from the establishment of an equilibrium between PPAHs and DPAHs.

It should be noted that the level of PPAH pollution in 2010 was similar to that in 2009, that is, there have been no annual variations in PAH concentrations. Furthermore, the 2009 PPAH concentrations obtained in 2010 for the shelf waters were higher than those in the deep-sea waters (Chizhova et al. 2013a).

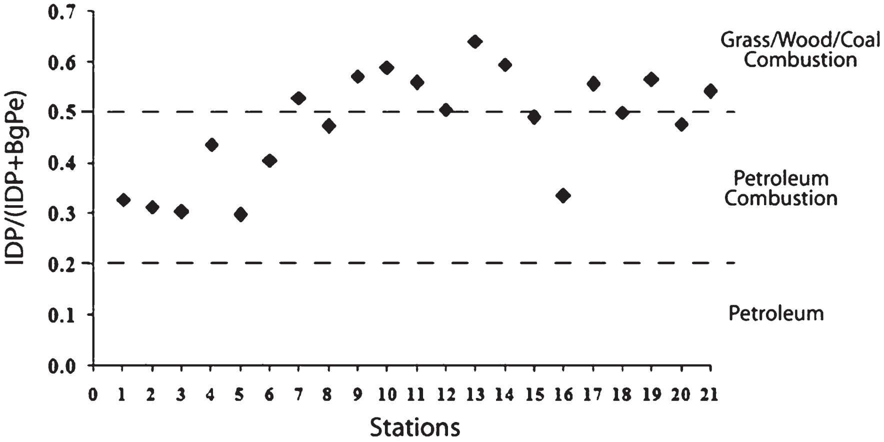

Fig. 14.8 IDP/(IDP + BgPe) diagnostic ratio versus sampling stations in July 2009

To determine the PAH sources in the Japan Sea, we used the PAH isomer pair ratios Flu/(Flu + Pyr) and IDP/(IDP + BgPe) with the highest stability order, which is a required factor for the identification of PAH origins in aquatic environments distant from PAH sources (Yunker et al. 2002; Tobiszewski and Namiesnik 2012). To calculate the ratio, a number of scientists have recommended using the sum of DPAHs and PPAHs (Tobiszewski and Namiesnik 2012).

As we studied PPAHs only in July 2009, we used the ratio IDP/(IDP + BgPe) to identify the origin of the PAHs. This is because IDP and BgPe are usually associated with suspended particulate matter due to the reduction in PAH dissolubility with an increase in the number of benzene rings (Neff 2002; McGowin 2006). Estimated ratio values demonstrate that petroleum combustion is the main source of PAHs in the western part of the sea (st. 1–8, Fig. 14.8). This PAH origin can be attributed to transportation activities in the surrounding areas, which has been confirmed by studies (Kakimoto et al. 2002; Ji et al. 2007) showing that fossil fuel combustion is the main source of PAHs in the atmosphere over cities located in the southwestern regions of Japan.

A study of the northeastern part of the sea (st. 9–21) has shown that the combustion of coal and wood is the major source of PAHs (Fig. 14.8). The main sources of PAHs in the region are forest fires in the Far East territories (Ding et al. 2007) resulting in fume transfer by continental winds in the spring and likely also in the beginning of summer. In fact, according to the European Space Agency (http://due.esrin.esa.int/), forest fires were registered in the vast areas of the northeastern part of China and the north regions of Primorye between May and June 2009.

Since we studied both PPAHs and DPAHs in the NWJS surface water in 2010, we used two ratios, Flu and IDP, to determine the PAH source. As a result of these calculations, we obtained indication of diverse PAH origins. The sources of the PAHs from the ratio Flu/(Flu + Pyr) were fossil fuels (petroleum, coal, etc.) at all sampling stations, except for station C2, where PAHs originated from petroleum

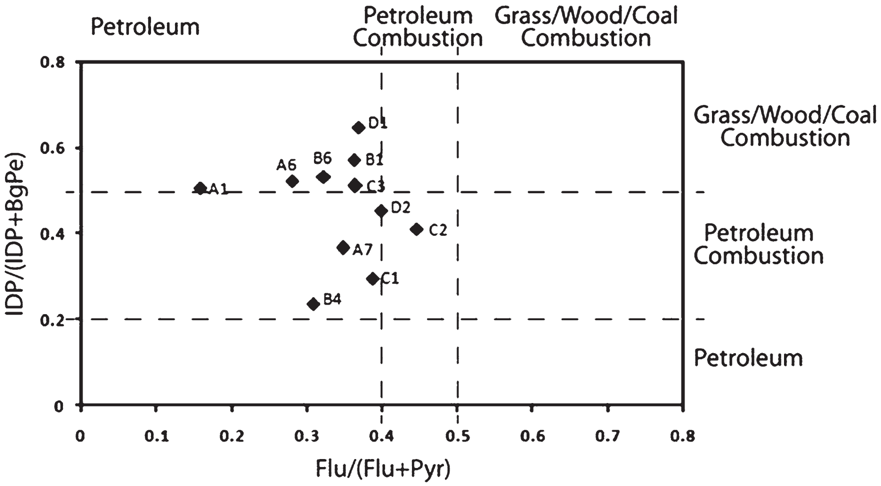

Fig. 14.9 Plot of PAH isomeric ratios in the NWJS surface water in Aug. 2010

combustion (Fig. 14.9). This finding can be attributed either to the petrogenic origin of most of the PAHs or to the lower ratio values due to Flu degradation. Flu is less stable to microbiological destruction than Pyr (Mackay et al. 2006). Based on the ratio IDP/(IDP + BgPe), stations close to zones of maximum anthropogenic influence in the regions C1, C2, and D2 had PAHs originating from petroleum combustion, while at the other stations, combustion of grass/wood/coal was the major contributor (Fig. 14.9).

Comparing the findings with PAH concentrations in other water areas, we note that the PAH concentrations in the studied regions of the Japan Sea were lower than those in the studied seas of East Asia and the Sea of Azov, and the PAH concentrations in the Kara Sea were lower than those in our studies (Table 14.4). At the same time, the DPAH concentration in the Mediterranean Sea near the coast of France was comparable to our findings for the Japan Sea. A comparison of the individual PAH concentrations obtained during our studies with those in the global scale presented previously (Wang et al. 2013) suggests that PAH pollution levels in the NWJS may be considered to be low. On one hand, low PAH levels in the NWJS can be caused by lower anthropogenic impact compared to that in Asian and European seas; on the other hand, the PAH study areas in the Japan Sea are located at a considerable distance from the coast, in contrast to studies in other water areas presented in Table 14.4.

Thus, studies of the spatial and temporal dynamics of PAHs in surface waters of the NWJS basin have shown an unequal distribution of the pollutants. PAH contamination in the coastal zones was directly related to the extent of industrialization and transport activities; pollution levels were reduced with distance from the coast, which are places of PAH localization. At present, it can be concluded that the NWJS is low or moderately polluted compared to the water areas of southern

Table 14.4 Reported PAH concentrations in the particulate and dissolved phases in the Japan Sea and world wide

Research area	Year	N	DPAH, ngL^{-1}	PPAH, ngL^{-1} or ngg^{-1}*	Predominant PAHs	References
East China Sea	2005, Nov.	10	70.2–71.4		Nap, Acy	Ren et al. (2010)
			30.4-85.1		Acy, Nap, BaA	
South China Sea			120.3		Nap, Acy, BaA	
Between seas						
South Yellow Sea	–	–	15.8–233.4		–	Han et al. (2009)
Azov Sea	2000–2007	16	20–350		Nap, Flu, triphenylene, Phe	Pavlenko et al. (2008)
Kara Sea	2007, Sept.	10	0.4–2.5		Phe	Nemirovskaya (2010)
Western Taiwan Strait, South China Sea	2009, June	15	12.3–58.0	10.3–45.5 (mean 15)	DP: Flu, Phe	Wu et al. (2011)
			(mean 19.8)		PP: Phe, Pyr	
Mediterranean Sea	2011, June-July	17	7.8–8.9 (5 stations), 41 (1 st.)	–	Nap, Phe, Ace, Fle, Pyr	Guigue et al. (2014)
Japan Sea	2009, July	13	–	1.2-4.4 193–2447*	Ace, Pyr, Fle, Flu	Chizhova et al. (2015)
Japan Sea	2010, Aug.	13	4.8–6.5	2.1–3.7 454–2418*	DP: Fle, Pyr, Ace, Flu	Chizhova et al. (2013a)
					PP: Ace, Pyr, Fle, Flu	

[a] TPAH concentration (DPAH+PPAH), ngL^{-1}
*means ngg^{-1}

Europe and Asia. Seasonal variability has been found in coastal water areas, for example, rising PAH concentrations in winter caused by emissions from central heating stations and domestic heating. It should be noted that annual variabilities in PAH concentrations have not been observed in surface waters of the open sea.

14.3 PAHs in the Water Column

Water columns are key components of the natural environment, where persistent organic pollutants are transported and undergo transformations before their deposition in the bottom sediments. To study the distribution of PAHs in the water column of the Japan Sea, we sampled DPAHs and PPAHs from different depths (from 0 to 3500 m) at two deep-sea sites during three cruises: at St. 1, the sampling was in July 2009 (here designated as La-46) and at St. 2, in August 2010 (La-51) and November

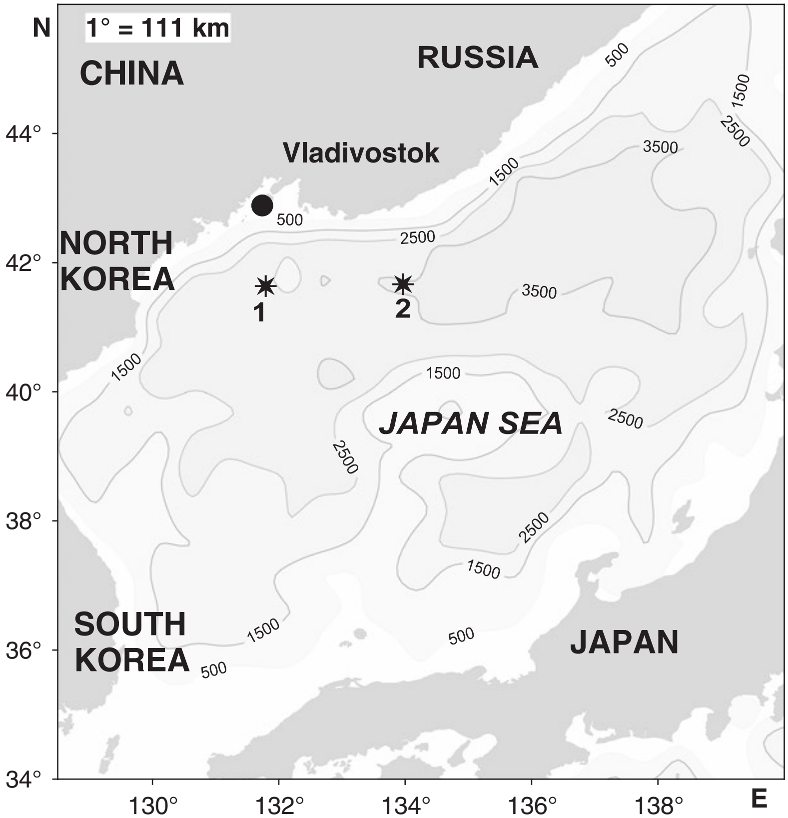

Fig. 14.10 Location of the sampling sites in 2009–2011. Depth at St.1 was 3289 m and at St. 2–3477 m

Table 14.5 Mean concentrations of dissolved and particulate PAH in the NWJS water masses (ngL^{-1})

	DPAH		PPAH		
Water layer	La-51	La-58	La-46	La-51	La-58
Surface (0–10 m)	5.76	30.77	3.05	2.13	0.92
Intermediate (10–500 m)	5.17	26.72	3.03	5.31	1.41
Deep (500–2700 m)	4.68	18.19	2.59	2.73	0.84
Bottom (2700 m-up to bottom)	4.39	15.62	2.72	3.04	0.81

2011 (La-58) (Fig. 14.10). The results of La-51 have been partially presented by Chizhova et al. 2013c.

The Japan Sea is generally vertically subdivided into intermediate, deep, and bottom water masses (Talley et al. 2006). The mean concentrations of DPAHs and PPAHs observed in these waters are presented in Table 14.5. It should be noted that the PPAH concentrations obtained at La-58 are considerably lower than the summer

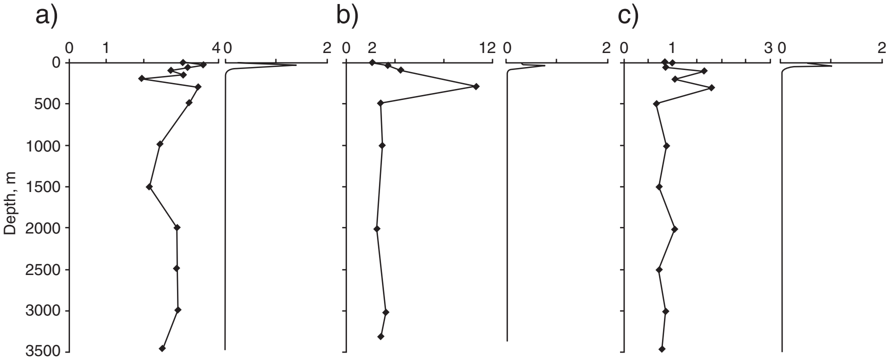

Fig. 14.11 Depth profile of PPAH (ngL^{-1}) and fluorescence of chlorophyll a (CTD data) in (**a**) July 2009 (La-46), St. 2; (**b**) Aug. 2010 (La-56), St. 1 and (**c**) Nov. 2011 (La-58), St. 2

results. These data contradict the seasonal trend of PAH occurrence in this region. This may be attributed to the different pretreatment methods used for the La-46, La-51, and La-58 samples, as mentioned above (see commentary to Table 14.2).

Concentrations of $\sum_{13}$PPAHs obtained in the water column ranged between 1.96–3.6 ngL^{-1} for La-46, 2.1–10.6 ngL^{-1} for La-51, and 0.73–1.8 ngL^{-1} for La-58 (Fig. 14.11), and three- to four-ring PAHs were predominate through the depth in all the cruises. Although the depth profile of PPAHs was irregular, there was no significant difference found in the concentrations of surface and near-bottom PPAHs. Sharp variations in the concentrations (three- and four-ring PAHs are predominant) occurred in the intermediate water layer as follows: 1.96–3.6 ngL^{-1} (La-46), 2.8–10.6 ngL^{-1} (La-51), and 0.7–1.8 ngL^{-1} (La-58). In the deep waters, concentrations of $\sum_{13}$PPAHs almost did not vary, except for La-58, where a decrease in the PPAH concentration was observed at depths of 1000 to 1500 m. In all the cruises, maximum concentrations of $\sum_{13}$PPAHs were found in the intermediate water layers (from 10 to 500 m). At La-46, the highest concentrations were observed at depths of 33, 150, and 300–500 m. At La-51, the PAH concentrations showed an increasing trend at the depth of 40 m and reached a maximum at 300 m. For the autumn samples (La-58), there were two distinct peaks found at depths of 100 and 300 m.

Because of their hydrophobic nature, PAHs tend to associate with suspended matter, the main source of which in the pelagic zones is phytoplankton. Several studies have shown that phytoplankton biomass-adsorbing PAHs is one of regulators of PAH settling and atmosphere-water exchange (Dachs et al. 2002; Berrojalbiz et al. 2011 and references therein). In fact, the PAH peak obtained at 33 m at La-46 corresponds to recorded levels of subsurface chlorophyll during the cruise (Fig. 14.11). However, similar apparent PPAH peaks were not found at La-51 and La-58, though a higher PAH content was observed at this depth compared with that in deep-water mass. One reason for this PAH behavior may be related to the amount of phytoplankton, which was less abundant in La-51 and La-58. Nevertheless, in the Japan Sea, the interaction between phytoplankton and hydrophobic pollutants requires more detailed study in the future.

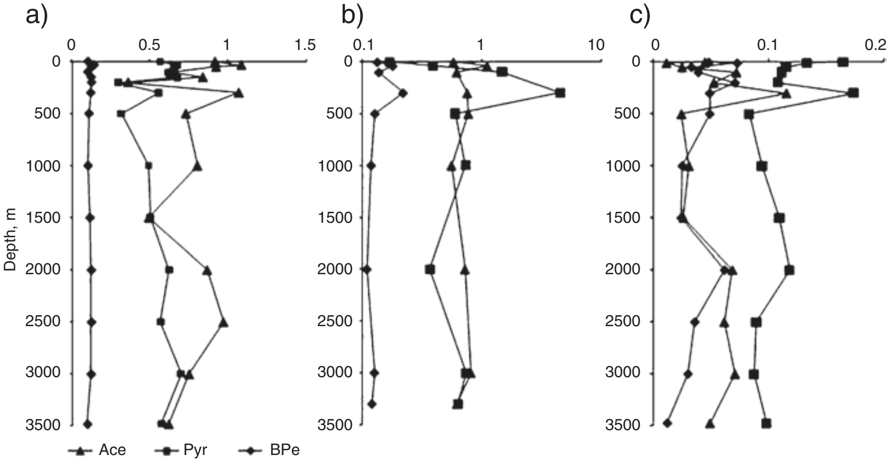

Fig. 14.12 Depth profile of some PPAHs (ngL^{-1}) at (**a**) La-46 (St. 2, July 2009); (**b**) La-51 (St.1, Aug. 2010), logarithmic scale; (**c**) La-58 (St. 2, Nov. 2011)

Zooplankton also participates in concentrating hydrophobic pollutants in the water column by both passively adsorbing the compounds and acquiring them during feeding (Berrojalbiz et al. 2009). A number of studies show the considerable role of zooplankton fecal pellets in the vertical transportation of PAHs (Prahl and Carpenter 1979; Lipiatou et al. 1993). In the central part of the Japan Sea, zooplankton as the dominant species are known to be able to descend to the mesopelagic zone (up to 200 m) in summer and accumulate in the 100–500 m layer in autumn (Dolganova and Stepanenko 2000). Thus, the $\sum_{13}$PPAH maxima we found in the layer of 100 to 500 m in the summer and autumn cruises are related to the zooplankton and their activity. It should be noted that the increased detection of PAHs in summer at a depth of 300 m (La-46 and La-51) is located below the main zooplankton population habitat. This can be associated with more deep-dwelling zooplankton population activity or the transfer of the main zooplankton pool's fecal pellets to the deeper-water zones due to variation in the hydrological features of the studied area (Ayukai and Hattori 1992). Consequently, tendencies for the concentration and dispersion of PPAHs in the water column are mostly associated with the "biological pump" activity. However, with respect to individual PAH distributions (Fig. 14.12), their behavior is more variable due to the physical and chemical properties of these compounds, the nature of the PAH-carrier particles, and many other factors.

Concerning DP, at La-51 and La-58, $\sum_{13}$PAH ranged between 4.3–6.5 and 13.7–35.4 ngL^{-1}, respectively (Fig. 14.13). Such a large difference in the concentrations found during these two cruises requires additional investigation. However, one may suggest that seasonal variability in the hydrographic conditions and the intensity of PAH transport over the sea surface by air masses, which is associated with northern monsoons and an increased concentration of PAHs in winter, could be one of the

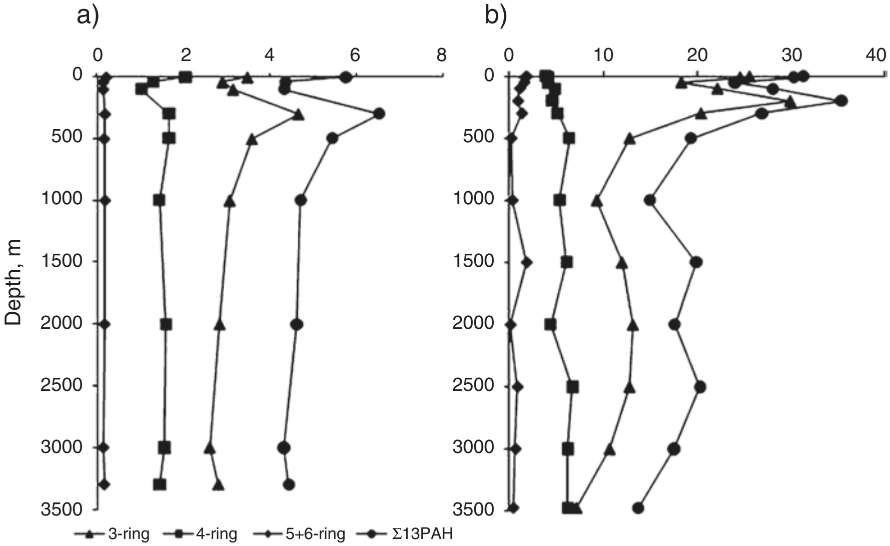

Fig. 14.13 Depth profile of DPAHs (ngL^{-1}) at (**a**) La-51 (St.1, Aug. 2010); (**b**) La-58 (St. 2, Nov. 2011)

reasons. Also, these two cruises show different PAH vertical profiles with depth. At La-51, there was no significant variation in the concentration with depth, except for two peaks: one in the surface and the other in the 300 m water layer. At La-58, high concentrations in the surface waters and at 200 m were recorded. Then, from 500 m to the bottom, the $\sum_{13}$PAH concentration decreased twofold due to a loss in three-, five-, and six-ring PAHs. In contrast, four-ring PAHs tended to increase toward the bottom (Fig. 14.13). DPAHs are considered to be more degradable by bacteria (Ghosal et al. 2016), and thus their concentration should decrease with depth. However, there was no such depth-depletion pattern found at St. 1. Lohmann et al. (2006) suggested that the fate of the dissolved pollutants compared with the suspended matter forms depends on the hydrological regime to a greater extent. As St. 1 was located closer to the area of slope convection occurrence than St. 2, its waters are assumed to be more frequently renewed (Talley et al. 2003; Tishchenko et al. 2003). Consequently, the substitution of waters with depleted PAHs for waters with relatively "fresh" pollutants occurs here with more intensity. In the more "conservative" waters of St. 2, significant degradation of low-molecular weight DPAHs with depth was observed. At the same time, a simultaneous increase in four-ring PAHs could be related to the aging of suspended matter and its release of PAHs.

The maximum DPAH concentration in the surface water layer can result from the leaching of incoming PAHs from the atmospheric suspended matter and following accumulation in this water layer. Additionally, atmospheric gaseous PAHs can contribute to pollution here. Peaks in the intermediate waters of both stations may originate due to PAH transitions in the dissolved phase during fecal pellet remineralization. In addition, these peaks could be caused by the different mechanisms of intermediate water formation (Talley et al. 2006). Thus, low-salinity intermediate water (100–150 m) is formed by the subduction of surface water from the northern part of the sea, where the PAH content is low. On the other hand, high-salinity intermediate water (200–500 m) is formed by winter convection (vertical mixing) involving water from the southern part of the sea, where the PAH content is rather high. The low concentration of PAHs below 500 m could be explained by the much slower renewal of water masses at this depth.

Finally, the highest level of PAHs in the Japan Sea water column is in the surface and intermediate waters. The vertical distribution of DPAHs and PPAHs is regulated by numerous biogeochemical, hydrological, and other processes. However, the cycling of PPAHs is associated, to a greater extent, with biogenic carbon flux.

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Chapter 15
Polycyclic Aromatic Hydrocarbons in the Southeastern Japan Sea

Kazuichi Hayakawa

Abstract Polycyclic aromatic hydrocarbons (PAHs) are one of many marine contaminants. Surface water samples were collected at 15 sites in the southeastern Japan Sea along the Japanese archipelago, and PAHs were found in the dissolved phase (DP) and particulate phase (PP). The mean total (DP + PP) PAH concentrations ranged from 6.83 to 13.81 ng/L. The mean PAH concentrations in the DP and PP were 5.99 and 3.38 ng/L, respectively. Three-ring PAHs predominated in the DP, while the proportion of four-ring PAHs was higher in the PP. The mean total PAH concentrations in the southeastern Japan Sea were higher than the concentrations in the northwestern Japan Sea. The Tsushima Current, which originates from the East China Sea, has higher PAH concentrations and is considered to be responsible for this higher concentration in the northwestern Japan Sea.

Keywords Polycyclic aromatic hydrocarbon · Japan Sea · Tsushima Current · Source

15.1 Introduction

The much higher atmospheric concentrations of PAHs and NPAHs in China, relative to Japan, mean that there are two possible major routes for their deposition in the Japan Sea. One is the current flow and the other is the wind flow. Also accidental oil spills are a third possible cause for the pollution in the Japan Sea, because crude oil contains many kinds of PAHs. However, little is known about the behavior of PAHs in the Japan Sea.

The Japan Sea is a virtually closed ocean system because all of the straits connecting it with other seas are narrow and shallow, having an average depth of 1350 m. The maximum depth of the Japan Sea is more than 3700 m. The Tsushima

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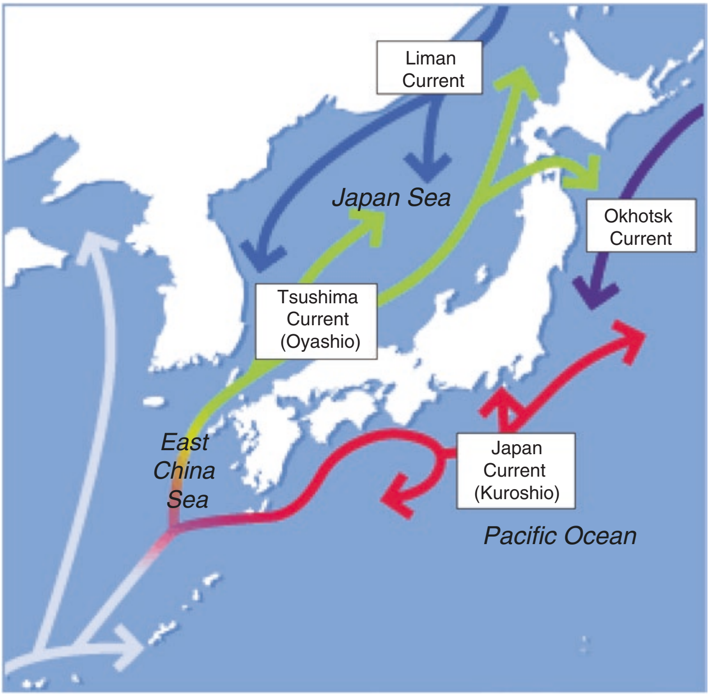

Fig. 15.1 Marine currents in the Japan Sea

Current (warm current) and the Liman Current (cold current) largely control water circulation in the Japan Sea. The warm current from the East China Sea is divided into two flows by the Japanese archipelago. One is the Tsushima Current, which flows into the Japan Sea through the Tsushima Strait. The other is the Kuroshio Current, which flows into the northwest of the Pacific Ocean. The Tsushima Current flows along the west coast of the Japan islands, while the Liman Current flows along the coast of Far Eastern Russia, and water flows out of the Japan Sea through the Tsugaru and Soya Straits (Fig. 15.1). Chapters 14 and 15, respectively, deal with the PAH distribution in the northwestern and southeastern Japan Sea, while PAH contamination from oil tanker spills in the Japan Sea is covered in Chap. 16.

15.2 Seawater Sampling and PAH Quantification

Surface water samples (about 10 L) were collected in August 2008 at 15 sites with a geographic range from 32°56′N, 128°6′E (site 1) to 43°5′N, 139°47′E (site 15) in the southeastern Japan Sea (Fig. 15.2). Acenaphthylene-d_{10} (Ace-d_{10}), pyrene-d_{10}

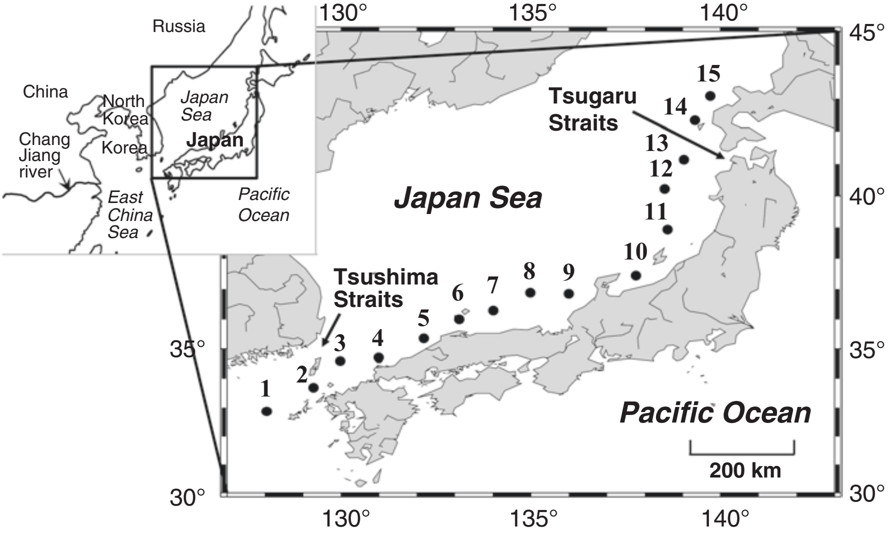

Fig. 15.2 Sampling sites in the southeastern Japan Sea

(Pyr-d_{10}), and B[*a*] P-d_{12} were used as internal standards for PAH quantification. Each surface water sample was filtered through a glass fiber membrane (pore size 0.5 μm), and the dissolved phase (DP)-PAHs and the particulate phase (PP)-PAHs were collected. The DP fraction (3 L) was spiked with the internal standards and subjected to solid phase extraction using a C_{18} cartridge. Both the C_{18} cartridge (containing DP-PAHs) and glass fiber membrane (containing PP-PAHs) were stored in a freezer at −20 °C until analysis. The DP-PAHs were eluted from the C_{18} cartridge with dichloromethane, and the solution was evaporated. The residue was dissolved in *n*-hexane and applied to a silica-gel cartridge. After washing the cartridge with *n*-hexane, PAHs were eluted using a mixture of *n*-hexane–acetone. The eluate was evaporated, and the residue was dissolved in acetonitrile for HPLC analysis. PP-PAHs were extracted by passing dichloromethane through a glass fiber membrane. The solution was spiked with the same internal standard solution as was added to the DP fractions. 100 μL of DMSO was added to the solution, and then the mixture was evaporated. The residue was dissolved in *n*-hexane, and the solution was applied to a silica-gel cartridge in the same manner as described above for DP-PAHs. The eluate from the cartridge was evaporated, and the residue was dissolved in acetonitrile for HPLC analysis. The HPLC system consisted of an ODS analytical column and a fluorescence detector. The mobile phase was a mixture of acetonitrile and water. Thirteen PAHs were quantified: acenaphthylene (Ace), fluorene (Fle), anthracene (Ant), fluoranthene (Flu), Pyr, benz[*a*]anthracene (B[*a*]A), chrysene (Chr), benzo[*b*] fluoranthene (B[*b*]F), benzo[*k*]fluoranthene (B[*k*] F), B[*a*]P, dibenz[*a*,*h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe), and indeno[1,2,3-*cd*]pyrene (IDP).

15.3 PAH Concentrations and Distributions in DP and PP

The DP-PAH, PP-PAH, and total PAH (T-PAH) concentrations in the southeastern Japan Sea are shown in Fig. 15.3 where the concentrations were not constant. The T-PAH concentrations ranged from 6.83 to 13.81 ng/L with a mean concentration of 9.36 ng/L (Fig. 15.3a). The PAH concentration in the DP fraction (DP-PAH) ranged from 3.71 ng/L to 10.01 ng/L with a mean concentration of 5.99 ng/L (Fig. 15.3b), and the PAH concentration in the PP fraction (PP-PAH) ranged from 2.18 ng/L to 4.58 ng/L with a mean concentration of 3.38 ng/L (Fig. 15.3c). Of the T-PAH concentration, the DP-PAH concentration accounted for 63.9%, suggesting that differences in the T-PAH concentrations are mainly caused by differences in DP-PAH concentrations. In the T-PAH, the most abundant PAH was Fle, followed by Ace. In the DP fraction, the most abundant PAH was Fle followed by Ace. Classified by the number of rings, three-ring PAHs (Ace, Fle, and Ant) accounted for 86.2% of the PAHs in the DP fraction. In the PP fraction, the most abundant PAH was Fle, followed by Pyr, which is different from the pattern found in the DP fraction. As a possible reason for the differences in PAH composition between the DP and PP fractions, the difference in vapor pressures of PAHs associated with the ring numbers is considered. The vapor pressure of Ace, a three-ring PAH, is 3.86 Pa, while the vapor pressure of four- to six-ring PAHs is in the range of 1.08×10^{-3} Pa (Flu) to 2.80×10^{-9} Pa (DBA) (Kim et al. 2013; Fu and Suuberg 2011). Accordingly, the water solubility of PAHs decreases with increasing ring numbers (Feng et al. 2007). The transferring mechanism of PAHs between water bodies and the atmosphere consists of the gas and particulate phases. Based on these characteristics, three-ring PAHs exist in the gas phase in the atmosphere, four-ring PAHs exist in both gas and particulate phases, and PAHs having five rings or more exist only in the particulate phase in the atmosphere (Araki et al. 2009). This difference suggests that gas phase PAHs dissolve in the seawater to be part of the DP-PAHs and particulate phase PAHs fall into the sea surface to be part of the PP-PAHs. These two pathways can explain the different PAH compositions between the DP and PP fractions.

Several PAH pairs have been identified for use as markers to identify the source of PAHs in natural water systems (Yunker et al. 2002). The ratio of [Flu]/[Flu + Pyr] < 0.4 implies petroleum leakage, while 0.4 to 0.5 implies petrogenic combustion, and >0.5 implies grass, wood, or coal combustion. Similarly, the ratio of [B[*a*]A]/[B[*a*]A + Chr] < 0.2 implies petroleum leakage, while 0.2 to 0.35 implies petrogenic combustion, and >0.35 implies grass, wood, or coal combustion. We calculated these values of the DP fractions at 15 sites to determine the sources. The [Flu]/[Flu + Pyr] and [B[*a*]A]/(B[*a*]A + Chr) ratios were in the range between 0.77 to 1.00 and 0.35 to 0.96, respectively, suggesting grass, wood, or coal combustion was a major contributor to the DP-PAHs. For the PP fractions, the [Flu]/[Flu + Pyr] ratios were in a wide range < 0.6, and the [B[*a*]A]/[B[*a*]A + Chr] ratios were in the range < 0.35, suggesting not only pyrogenic origins but also petroleum origins such as oil from ships. The PP-PAH concentrations lower than the DP-PAH concentrations

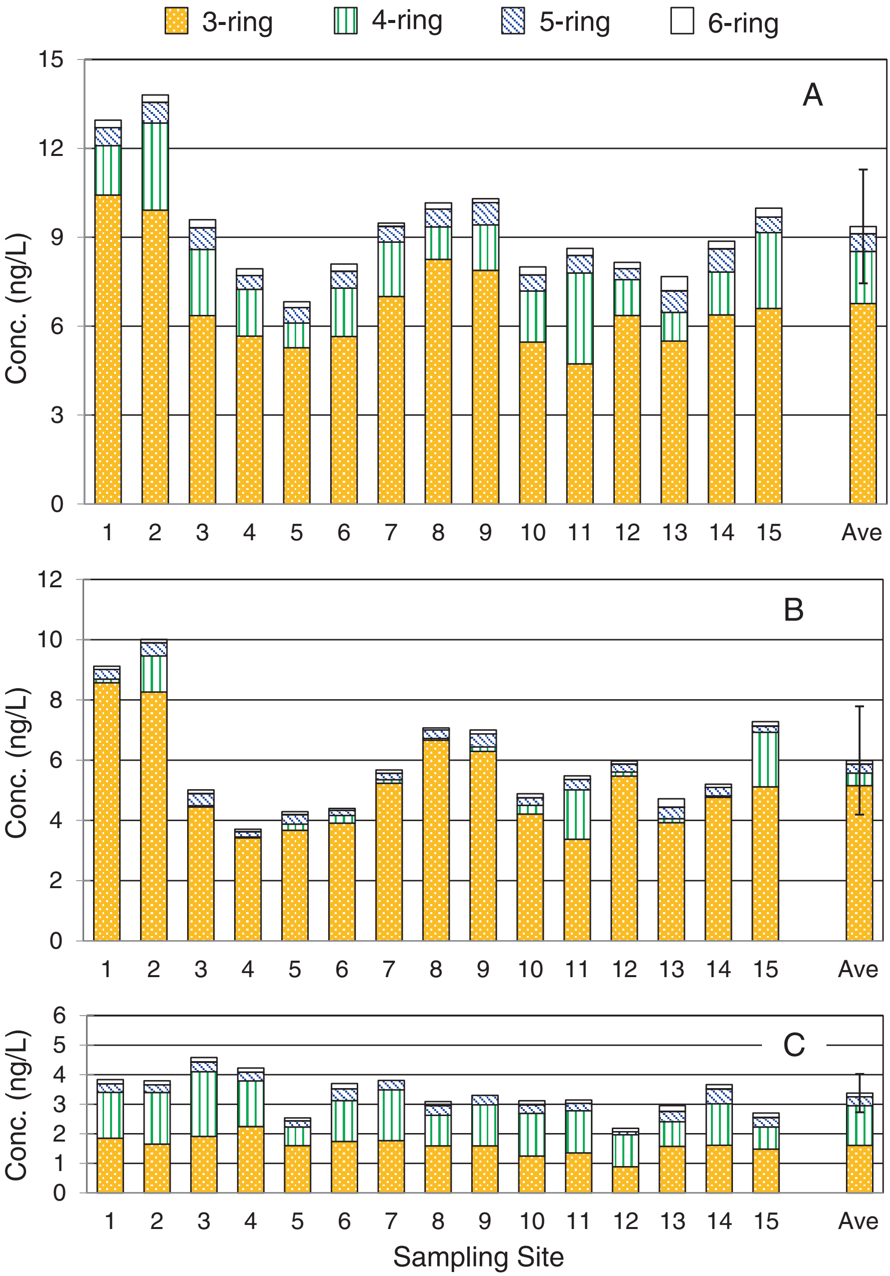

Fig. 15.3 Concentrations of PAHs at 15 sampling sites (**a**) total (DP + PP) PAHs, (**b**) DP-PAHs, (**c**) PP-PAHs

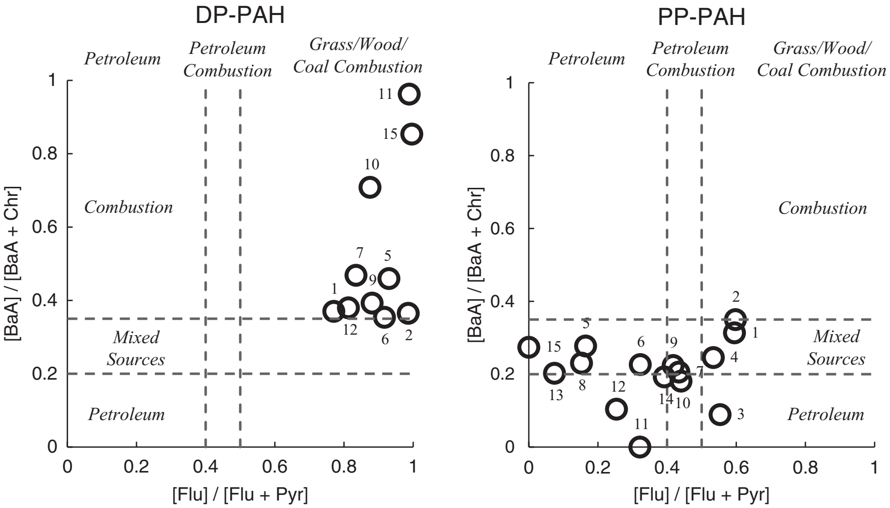

Fig. 15.4 Source estimation of PAHs in the southeastern Japan Sea
DP, dissolved phase; PP, particulate phase. Data from sites 3, 4, 13, and 14 are not plotted for the DP-PAH because Flu was below the quantification limit

(Fig. 15.4) suggest that the contribution from petroleum is smaller than that of combustion emissions. Both DP and PP-PAHs in the northwestern Japan Sea showed ratios of [Flu]/[Flu + Pyr] in the range of 0.2–0.4, while the ratio of [B[*a*]A]/[B[*a*]A + Chr] was 0.4–0.9 and 0.2–0.6 for the DP- and PP-PAHs, respectively (Chizhova et al. 2013). These values suggest mixed sources of inputs from both pyrogenic and petroleum origins for PAHs in the northwestern Japan Sea. PAHs in the southeastern Japan Sea were considered to be of similar origins to PAHs in China, which increased significantly in winter as a result of coal burning for heating (Yang et al. 2007).

15.4 Comparison Between PAH Distributions in the Southeastern Japan Sea and Other Seas

The mean total (DP + PP) PAH (= T-PAH) concentration in the southeastern region (9.36 ng/L) was slightly higher than that of the northwestern region with concentrations that ranged from 7.4 to 10.2 ng/L and a mean of 7.9 ng/L (Fig. 15.5) (Chizhova et al. 2013). As a possible reason for the difference, the effect of currents is considered. The Liman Current (cold current) flows along the northwestern Japan Sea, and the Tsushima Current (warm current) flows into the southwestern region of the Japan Sea through the Tsushima Straits (Fig. 15.1). The Tsushima Current consists of waters from several large Chinese rivers. The Chang Jiang (Yangtze) River flows

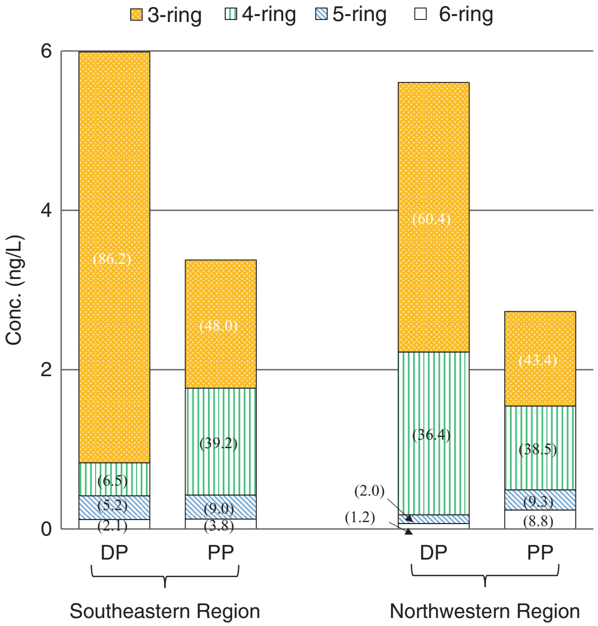

Fig. 15.5 Comparison of PAH concentration and composition between the southeastern and northeastern Japan Sea

DP, dissolved phase; PP, particulate phase. Numbers in parentheses indicate the percentage of three- to six-ring member PAHs in the DP and PP fraction. PAH concentrations in the northwestern Japan Sea are from a previous study (Chizhova et al. 2013)

into the East China Sea from highly populated areas of China where industries, power plants, domestic heating, and cooking use large amounts of fossil fuels. Combined with the burning of biomass in agriculture, they comprise the major sources of PAHs. The concentration of the T-PAHs in the Chang Jiang River (185.3 ng/L) was about 20 times higher than the concentration in the southeastern Japan Sea. Moreover, in the DP fraction, three-ring PAHs were the most abundant PAHs. This result corresponds with the PAH compositions of the southeastern Japan Sea (Fig. 15.3).

The Chang Jiang River flows into the East China Sea at the rate of 1×10^{12} tons/year and accounts for about two thirds of the effluent that flows into the Tsushima Straits area. On the other hand, the Liman Current originates from Far Eastern Russian rivers, such as the Amur River, which flow through much less populated areas than does the Chang Jiang River. Moreover, the flow volume of the Amur River (3.3×10^8 tons/year) is much less than that of the Chang Jiang River. Thus the Tsushima Current, polluted with PAHs, might increase the concentration of T-PAHs in the southeastern Japan Sea. This transport process of PAHs might explain the lower mean concentration of the T-PAHs in the southeastern Japan Sea compared to the East China Sea (70.22–120.2 ng/L) and the western Taiwan Strait (23.3–70.9 ng/L) (Wu et al. 2011).

The PAH pollution level of the Japan Sea can be compared to those of other seas, although the analyzed species are not the same. The total concentration of ten PAHs (Ace, Phe, Ant, Flu, Pyr, B[*b*]F, B[*k*]F, B[*a*]P, BPe, and coronene) in the open Atlantic Ocean was in the range of 0.06–1 ng/L (Nizzetto et al. 2008). The total concentration of eight PAHs (Flu, Pyr, B[*a*]A, Chr, B[*b*]F, B[*k*]F, DBA, and BghiPe) in the western Mediterranean Sea was 1.07 ng/L (Dachs et al. 1997). In contrast, the total concentration of 5 PAHs (Ace Fle, Flu, Pyr, and B[*a*]A) in the Gulf of Venice in the Adriatic Sea (9.62 ng/L) (Manoli and Samara 1999) was at the same level as that in the Japan Sea. Several recently published reports concerning PAH distributions in Asian seawater show that the concentrations of 16 PAHs in the PP and DP fractions of the surface seawater along the coast of Xiamen Island, China, were in the range of 28.2–128.7 ng/L (mean, 59.2 ng/L) and 62.0–341.9 ng/L (mean, 182.4 ng/L), respectively (Ya et al. 2014). The concentrations of seven PAHs in seawater along the Klang Strait, Malaysia, were in the range of 67.0–693.7 ng/L (Tavakoly et al. 2014). These results suggest that the Japan Sea and surrounding seas seem to be more polluted with PAHs than the Atlantic Sea and Mediterranean Sea. East Asian countries are developing quickly with increasing energy consumption. Pollution loadings from countries surrounding the Japan Sea, such as China, have increased significantly, and PAH contamination in seas adjoining the Japan Sea has been reported (Chen et al. 2007; Men et al. 2009; Ren et al. 2010). In order to predict future trends of PAH pollution and to take effective countermeasures against contamination in East Asian seas, continuous international collaborative observations are needed.

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Chapter 16
Oil Spills and Polycyclic Aromatic Hydrocarbons

Kazuichi Hayakawa

Abstract Crude oil contains many kinds of polycyclic aromatic hydrocarbons, and its release into the marine environment causes serious damage. It is important to understand the behavior and biological effects of PAHs as components of oil. Over the last five decades, many large-scale oil spills, including the Gulf War oil spill in 1991 and the Gulf of Mexico oil spill in 2010, have occurred in the world. This chapter describes the long-term impact on marine and coastal environments by C-heavy (the last distilled fraction of heavy oil) oil spilled from the Nakhodka in the Japan Sea in 1997, where polycyclic aromatic hydrocarbons were monitored as pollution markers.

Keywords Nakhodka oil spill · Heavy oil · Polycyclic aromatic hydrocarbon · Japan Sea · Fish

16.1 Introduction

Crude oil contains many kinds of hydrocarbons such as polycyclic aromatic hydrocarbons (polynuclear aromatic hydrocarbons, PAHs), asphaltene, and resin. Oil spills from ships and oil wells cause serious damage to marine and coastal environments. It is important to understand the behavior and biological effects of PAHs as components of oil. The 1967 Torrey Canyon oil spill in the Dover Strait led to international rules to prevent oil contamination. Since then, 13 large-scale oil spills, over 100,000 tons, including the Gulf War oil spill in 1991 and the Gulf of Mexico oil spill in 2010, have occurred (Moss 2016; Smithsonian National Museum of Natural History 2016). In those oil spills, several long-term environmental impact assessments, such as the 1989 Exxon Valdez oil spill in Alaska, have been carried out

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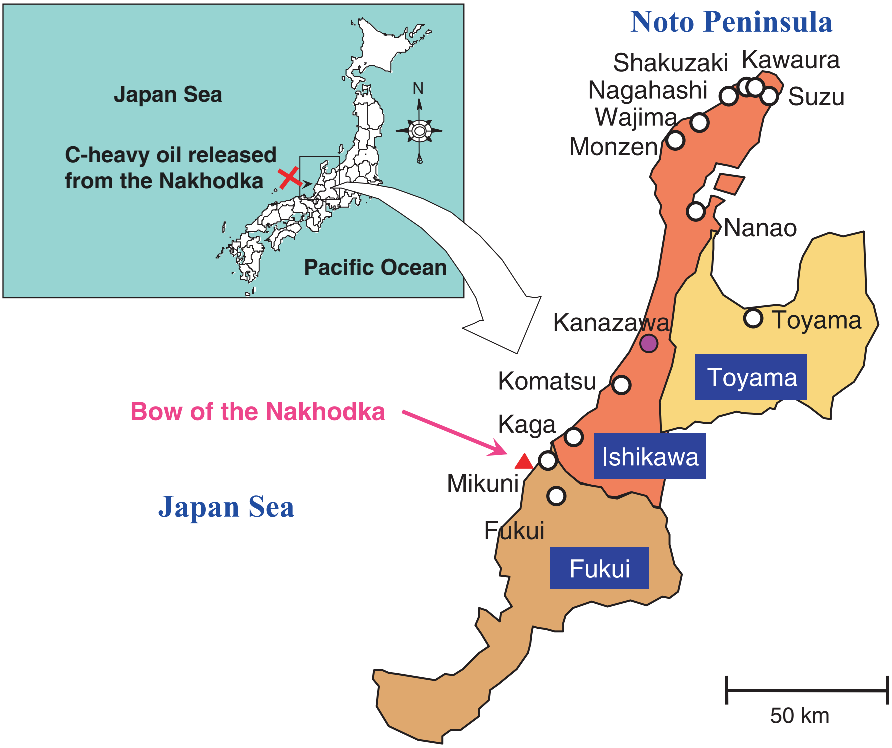


Fig. 16.1 Coastlines of Ishikawa and Fukui prefectures

(Maki 1991; Neff and Burns 1996; Davies and Toppong 1995; Wells et al. 1995). Most of these spills were crude oil spills.

A Russian tanker, the Nakhodka (13,157 gross tons), loaded with C-heavy oil, sank because of a strong northwest wind in the Japan Sea about 100 km offshore from Oki Islands, Japan, on January 2, 1997. Over 6000 kL of the loaded C-heavy oil leaked from the tanker, and a part of it was blown onto the Japanese coastlines from Shimane Prefecture to Akita Prefecture, Japan. The amount of beached C-heavy oil was significantly large on the coastlines of Fukui and Ishikawa Prefectures (Fig. 16.1). The Nakhodka oil spill was the third largest scale oil spill in the seas near Japan since 1970. After the spill, many people, including volunteers, attempted to clean up the spilled oil, and researchers from Japanese national and local governments and universities began environmental impact assessments.

Crude oil is distilled into gasoline, kerosene, light oil, heavy oil, and tar by increasing the temperature. C-heavy oil is the last distilled fraction of heavy oil. The concentrations of PAHs having four rings or more in C-heavy oil are much higher than in crude oil. This is the reason for the high viscosity and the longevity of C-heavy oil in the environment. It is well known that PAHs, such as benzo[*a*]pyrene, can act as carcinogens or mutagens. Because of this, PAHs in the blue mussel were investigated over a year after the Braer Corp crude oil spill in the Shetland Islands in 1993 (Webster et al. 1997). In addition, several metabolites of PAHs were found to show adverse effects to marine organisms. Several hydroxylated PAHs show agonistic and antagonistic activities in the estrogen receptor and disruption in bone metabolism in fish. Several PAH quinones cause the overproduction of reactive oxygen species (ROS) in cultivated cells (see Part VI). These results suggest both direct, indirect, long-, and short-term effects of spilled oil on marine and coastal ecosystems.

During the 2 years after the Nakhodka oil spill, the degree of oil contamination of coastlines in Ishikawa and Fukui Prefectures, Japan, was assessed. In addition, the recovery of the coastlines was monitored by examining PAHs in oiling lumps (oil ball and paste), sand, seawater, and fish.

16.2 Relationship Between Coastal Characteristics and Residual Tendency of C-Heavy Oil

Visual observations at coastlines contaminated with C-heavy oil from the Nakhodka were made on (1) March 21 and April 17–18, 1998 and (2) April 17–18 and May 15, 1999. The total length of the coastline investigated was 170 km, spanning from Suzu, Ishikawa Prefecture, to Mikuni, Fukui Prefecture (Fig. 16.1), with the exception of steep coasts which could not be reached by foot. The coastlines investigated were divided into 176 zones, and the amount of C-heavy oil was visually monitored. The substrates of the zones were classified into four types: bedrock (60 zones), boulder/cobble/pebble (particle size not less than 4 mm, 34 zones), gravel/sand (particle size <4 mm, 53 zones), and man-made material (concrete tetrapods, 29 zones). The shapes of the bedrock and boulder/cobble/pebble on the coasts were classified into three types: exposed (30 zones), pocketed (35 zones), and sheltered (32 zones).

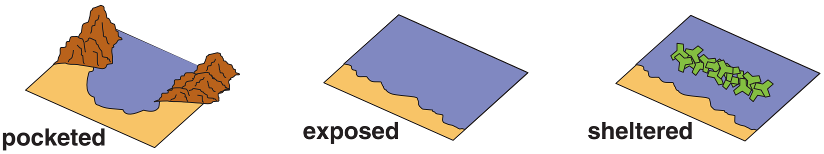
After 1 year of observation (approximately 14.5 or 15.5 months after the spill), 47% of bedrock sites, 47% of boulder/cobble/pebble sites, and 50% of man-made material sites were classified as heavily oiled (level D) coasts, but only 6% of the gravel/sand coasts were classified as heavily oiled (Table 16.1). After 2 years of observation (approximately 27.5 or 28.5 months after the spill), the percentage of the heavily oiled coasts was remarkably lower. The coastlines of the Noto Peninsula are mainly covered with bedrock or boulder/cobble/pebble, while coastlines of the south part of Ishikawa Prefecture (Kaga area) are mainly covered with sand (Fig. 16.2a). The heavily oiled coasts were mainly observed in the Noto Peninsula 1 and 2 years after the spill (Fig. 16.2b). A strong correlation was observed between the heavily oiled sites and bedrock or boulder/cobble/pebble areas. Unlike the contamination in the bedrock or boulder/cobble/pebble areas, the contamination of coastal gravel/sand or man-made materials rapidly recovered. This difference suggests that the tidal strength was strong enough to wash the coastal gravel/sand and man-made materials. The coastal shape also tends to affect how long oil remains. After 1 year of observation, the high percentages of heavily oiled coasts were observed at sheltered sites for the bedrock coasts and sheltered sites for the boulder/cobble/pebble coasts (Picture 16.1).

Table 16.1 Relationship between oiling level and habitat of Ishikawa and Fukui coastlines

Habitat	n	After 1 year %				After 2 years %			
		A	B	C	D	A	B	C	D
Rock	60	29	9	15	47	13	62	17	8
Boulder/cobble/ Pebble/gravel	34	12	21	21	47	44	27	18	12
Sand	53	59	19	16	6	68	22	4	6
Man-made	29	31	7	12	50	38	37	25	0

Observations: (after 1 year) March 21, 22 and April 17, 18, 1998; (after 2 years) April 17, 18 and May 5

Oiling levels: A, none remaining; B, light; C, moderate; D, heavy



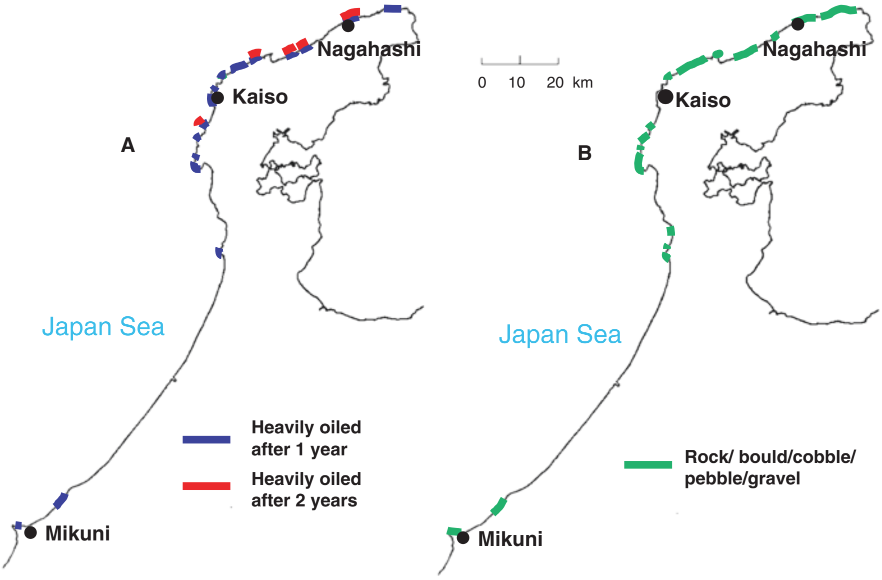
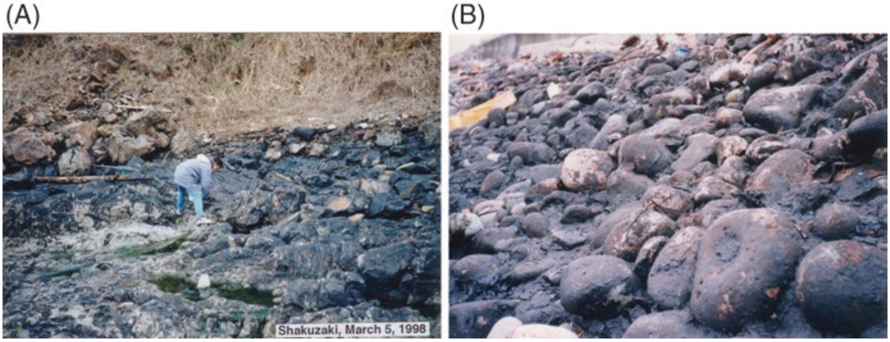


Fig. 16.2 Relationship between coastal characteristics and the longevity of C-heavy oil spilled from the Nakhodka. (**a**) Zones covered with bedrock or boulder/cobble/pebble, (**b**) heavily oiled zones at 1- and 2-year observations

The tendency for the oil to remain was also affected by meteorological conditions, topographic features, and physical properties of the oil. A large part of the coastlines of the Noto Peninsula are sheltered. The waves are usually weakened by offshore rocks. However, in the winter a strong northwest wind from the Asian continent hits the west coast of the Japan Islands, causing high energy waves to strike



Picture 16.1 Pictures of long-term heavily oiled coasts. (**a**) Shakuzaki, Suzu, on March 5, 1998. (**b**) Kawaura Beach, Suzu, on March 5, 1998

the coast. In January, waves in the Japan Sea may have deposited oil on the shores over the sheltered rocks. After C-heavy oil is beached, it may have been difficult to remove from either sheltered or exposed types of coasts because the oil hidden within the rocks and of its high viscosity makes contact with waves difficult. Other factors possibly affecting the length of time oil remains on the coasts of the Noto Peninsula might include the steepness of the shores, as well as the lack of volunteer effort due to an areas' remoteness. The above results made it possible to adopt suitable countermeasures including cleanup methods for each type of coast. For this purpose, the Hazardous Materials (HAZMAT) Response and Assessment Division of the US National Oceanic and Atmospheric Administration (NOAA) has published Environmental Sensitivity Index (ESI) maps which describe all environmental elements that mediate the extent of contamination, such as relative exposure to waves and tidal energy, shoreline slope, substrate type, biological productivity, and sensitivity (NOAA HAZMAT 2002). As a lesson from the Nakhodka oil spill, the Japanese Coast Guard made the ESI of the shorelines of Japan (Japan Coast Guard 2009). According to the guidelines, the fragility of coastal bedrock and boulder/cobble/pebble is higher than that of gravel/sandy beaches, and the fragility of sheltered-type coasts is higher than that of the exposed coasts.

16.3 PAHs in Oil Lumps, Sand, and Seawater

Samples of the beached oil, sand, and seawater were collected at five sites: Otani and Nagahashi (Suzu, Ishikawa), Fukami and Kaiso (Monzen, Ishikawa), and Sunset Beach (Mikuni, Fukui) (Fig. 16.1). Their substrate types and the shapes of the coasts of the five sampling sites are as follows: Otani (Suzu), sand, exposed; Nagahashi (Suzu), bedrock, sheltered; Fukami (Monzen), bedrock, pocket; Kaiso (Monzen), boulder/cobble/pebble, sheltered; and Sunset Beach (Mikuni), sand, exposed. Nakhodka C-heavy oil or beached oil lump was weighed, dissolved in benzene, and diluted with acetonitrile. Deuterated PAHs (naphthalene-d_8,

Table 16.2 Concentrations of PAHs in The Nakhodka C-heavy oil

Number of rings	Name	Concentration (μg/g)
2	Naphthalene	410
3	Acenaphthene	27
	Fluorene	106
	Phenathrene	2630
	Anthracene	33
4	Fluoranthene	47
	Pyrene	164
	Benz[*a*]anthracene	210
	Chrysene	336
5	Benzo[*b*]fluoranthene	92
	Benzo[*k*]fluoranthene	14
	Benzo[*a*]pyrene	91
	Dibenz[*ah*]anthracene	110
	Benzo[*ghi*]perylene	217
6	Dibenz[*ah*]anthracene	76

phenanthrene-d_{10}, pyrene-d_{10}, and benzo[*a*]pyrene-d_{12}) were added as internal standards to each sand sample, and PAHs were extracted with *n*-hexane. One half of the solution was evaporated to dryness and dissolved in acetonitrile. Each seawater sample was filtered with a membrane filter (pore size 0.4 μm), and deuterated PAHs were added to the filtrate as internal standards. The solution was applied to a polymethacrylate cartridge. PAHs on the cartridge were eluted with acetonitrile. An aliquot of each solution was injected into an HPLC system for PAH quantification. The 16 US EPA PAHs (minus acenaphthylene) were all detected in the Nakhodka C-heavy oil. Among these PAHs, phenanthrene (Phe), a three-ring PAH, had the highest concentration followed by chrysene (Chr), a four-ring PAH (Table 16.2).

The Nakhodka C-heavy oil contained not only PAHs having two to four rings but also PAHs having more rings such as indeno[1,2,3-*cd*]pyrene (IDP), a six-ring PAH. In aged lumps on the coasts, the concentrations of PAHs were lower than those in the Nakhodka C-heavy oil, suggesting the degradation of PAHs in the environment. Naphthalene (Nap), a two-ring PAH, rapidly disappeared after the spill (Fig. 16.3). By contrast, the decreases of the other PAH concentrations were much slower. This is because Nap (boiling point 217.9 °C, melting point 80.2 °C) is more volatile than PAHs having three rings or more. Nap sublimes easily even on cold winter days. The boiling point of anthracene (Ant) (342 °C), a three-ring PAH, is higher than that of Nap, which might explain why the concentration of Ant did not decrease soon after the spill but decreased gradually. Another reason for the fast decrease of Nap may be its relatively high solubility in seawater. The solubilities of PAHs in water are compared in Table 1.1 in Chap. 1. The solubility of Nap (19–38 mg/L in seawater at 22 °C) is much larger than that of benzo[*a*]pyrene (BaP) (0.003 mg/L in seawater at 22 °C), a five-ring PAH, in seawater (Verschuerene 2001).

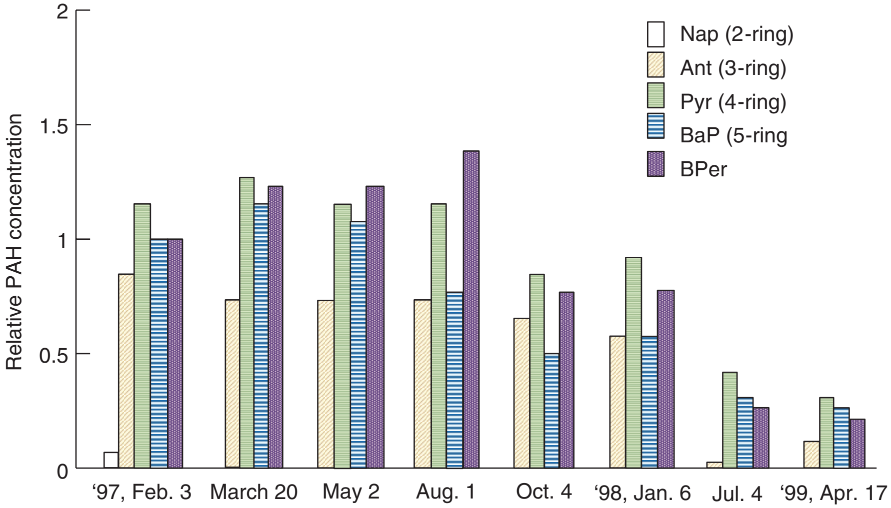


Fig. 16.3 PAH concentrations in beached oil lumps collected on bedrocks at Nagahashi, Suzu Each PAH concentration is the mean value of three samples and is expressed as a value relative to those in the Nakhodka C-heavy oil

Figure 16.3 shows the time course of concentrations of PAHs in beached oil relative to the concentrations in Nakhodka C-heavy oil. Both pyrene (Pyr), a four-ring PAH, and benzo[*ghi*]perylene (BghiPer), a five-ring PAH, increased up to August 1, 1997 (7 months after the spill) and then decreased. This initial increase of the concentrations of Pyr, BaP, and BghiPer might be due to evaporation of the components having low boiling points from the lumps. PAHs having four rings or more could not be easily degraded (Cookson 1995), although bacterial degradation of n-alkanes (Tazaki 1997) and PAHs having two or three rings have been reported (Hayakawa et al. 2000). These results suggest that the gradual decreases in the concentrations of Pyr, BaP, and BghiPer having four rings or more observed on the contaminated coastlines might be mainly due to photolysis (Tebbens et al. 1971). Moreover, among these three PAHs, BaP showed the fastest decrease in the first year, possibly because it is less stable in sunlight (Hayakawa et al. 2002).

The concentrations of BaP in seawater at Nagahashi (Suzu) and Kaiso (Monzen) were 7.5–8 μg/L on February 8, 1997 (1 month after the spill), and the concentrations at Sunset Beach, Mikuni, were lower on May 2, 1997 (4 months after the spill) than those at the other two sites because of the quick recovery operation described above. However, the concentration at Sunset Beach was as high as those of the other sites on January 6, 1998 (1 year after the spill), suggesting transportation of the contamination from other polluted sites. The concentrations decreased gradually at the three sites, reaching sub ng/L levels by April 30, 2000, more than 3 years (40 months) after the spill (Fig. 16.4).

BaP concentrations in seawater at three coasts (Nagahashi, Kaiso, and Sunset Beach) were compared to that of several other coasts that were not affected by the Nakhodka oil spill (Fig. 16.5). Surprisingly, the BaP concentrations in seawater at

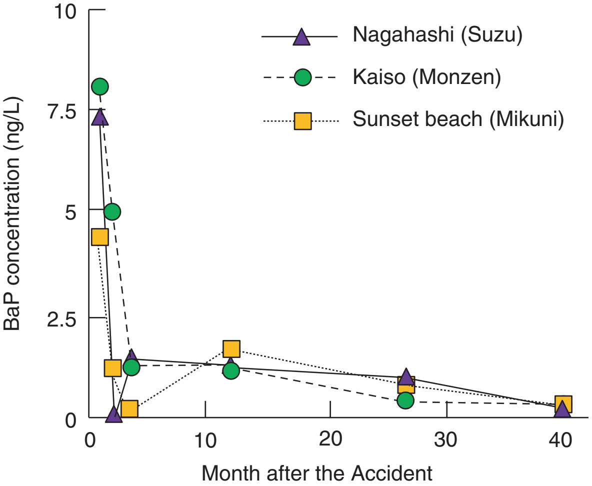


Fig. 16.4 BaP concentrations in seawater at Nagahashi (Suzu), Kaiso (Monzen), and Sunset Beach (Mikuni) after the Nakhodka oil spill
Each point and bar represents the concentration and SD, respectively
Sampling dates: February 8, March 20, May 2, 1997; January 6, 1998; April 17 (May 8 for Sunset Beach), 1999; April 30, 2000

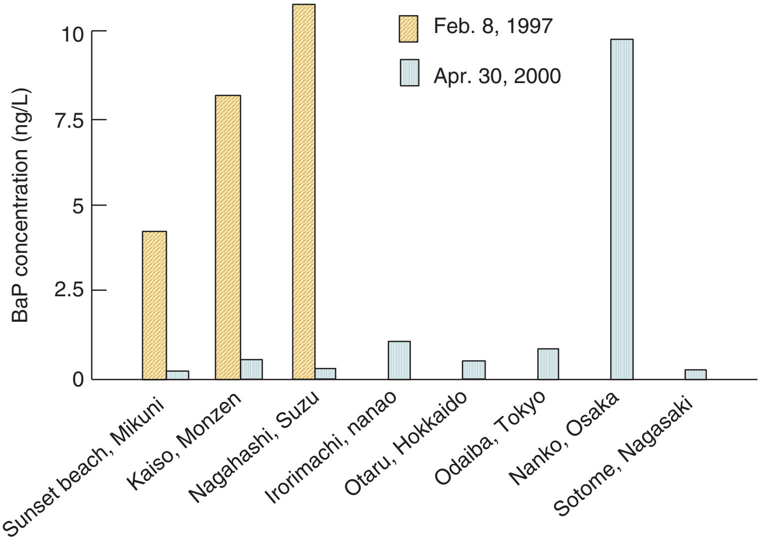


Fig. 16.5 Comparison of BaP concentrations in seawater at Nagahashi (Suzu), Kaiso (Monzen), and Sunset Beach (Mikuni) and other beaches in Japan
Each concentration represents the mean values of two samples

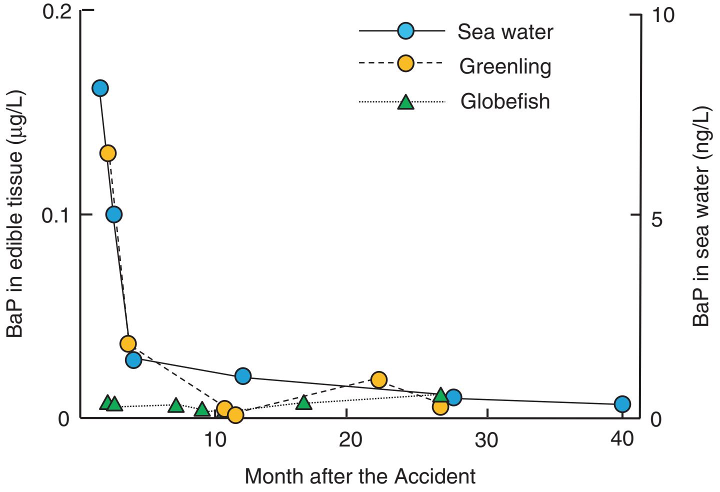


Fig. 16.6 BaP concentrations in edible tissues of greenling and globefish collected at Kaiso, Monzen, Japan, after the Nakhodka oil spill

the three beaches on February 8, 1998 (1 month after the spill) were comparable to that at Nanko, Osaka, whose harbor is well known for its pollution. However, on April 30, 2000 (more than 3 years after the spill), the BaP concentrations at the three coasts (0.20–0.27 ng/L) were as low as those at Sotome (Nagasaki) and Otaru (Hokkaido) which are famous for their cleanness. This suggests that the above three coasts all recovered from the seawater pollution by 3 years after the spill.

16.4 PAHs in Fish

Fish were collected at Kaiso, Monzen (Fig. 16.1), which had the highest BaP concentrations in seawater in the first 2 months after the spill in the three coasts as shown in Fig. 16.4. Two nonmigratory species, greenling and globefish, live in a narrow area near the shoreline, which was polluted with oil. The concentration of BaP in edible tissues of greenling was 0.13 ng/g on March 20, 1997 (2 months after the spill) which was much higher than that in globefish. The concentration was still higher on April 17, 1997 (3 months after the spill). On November 15, 1997 (more than 10 months after the spill), the concentration was as low as the level in unpolluted seawater (0.005 ng/g) (Fig. 16.6). The change in BaP concentrations in the edible tissues of greenling tended to follow the pattern change of BaP concentration in seawater, although the sample number was not large enough to obtain a clear conclusion. On the other hand, the concentration of BaP in edible tissues of globefish was not so high, possibly because this species lives on bedrock near the sea surface while greenling live at the bottom of the sea and/or because globefish do not have as much fatty tissue. Thus, the BaP in greenling might be a biomarker for C-heavy oil contamination of seawater.

High concentrations of PAHs in fish were also observed after the Exxon Valdez crude oil spill (Al-Yakoob et al. 1993). During 4 months after the Exxon Valdez oil spill, the total concentration of PAH subcomponents (naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) in tissues (6.9 + 1.4 μg/g) was much higher than that in the control (0.025 + 0.013 μg/g). The concentration in the pink salmon tissues (0.18 + 0.028 μg/g) was also much higher than that 1 year after the spill (0.051 + 0.007 μg/g) which was as low as the control level (Carls et al. 1996). The tendency for the PAH concentration in fish to be significantly higher just after the spill and to decrease to the control level in a year was similar to what we observed in greenling fish following the Nakhodka oil spill.

More detailed studies of oil on fish eggs and fishes are described in Part VI.

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Part VI
Metabolic Activation/Toxicities

Chapter 17
Metabolic Activation

Kanae Bekki

Abstract PAHs are metabolized by various drug-metabolizing enzymes within the body. Although xenobiotic metabolism is an essential physiological function for environmental chemical detoxification, it is possible that reactive metabolic intermediates are formed in some cases. For instance, metabolism of PAHs generates hydroxylated PAHs (OHPAHs) and PAH quinones (PAHQs), which respectively have estrogenic/antiestrogenic and oxidative stress activities. These metabolites have some functional groups, such as -OH and = O, and OHPAHs and PAHQs have numerous isomers. Previous reports show that these isomers have different degrees of toxicity. Therefore, we investigated the structural activity relationships between the position of functional groups and biological activities and show that several physical parameters such as L/B ratios and O-H distances contribute to the estrogenic/antiestrogenic activities of OHPAHs. In addition, these activities mainly depend on the position of substituted groups rather than on the kinds of functional groups. On the other hand, we found the structural activity relationship for PAHQs in the experiments measuring oxidative stress, cell viability, and ROS generation and show that *ortho*-PAHQs have stronger potential for ROS generation than *para*-PAHQs. These data suggest that the structural activity relationships of PAH derivatives could be roughly predicted from their physical parameters.

Keywords Hydroxylated PAHs · PAH quinones · Structural activity relationship

17.1 Introduction

Once PAHs are inhaled, these lipophilic compounds can easily cross cell membranes and be detoxified through several processes. For example, most PAHs are well known as activators of the aryl hydrocarbon receptor (AhR) – one of the

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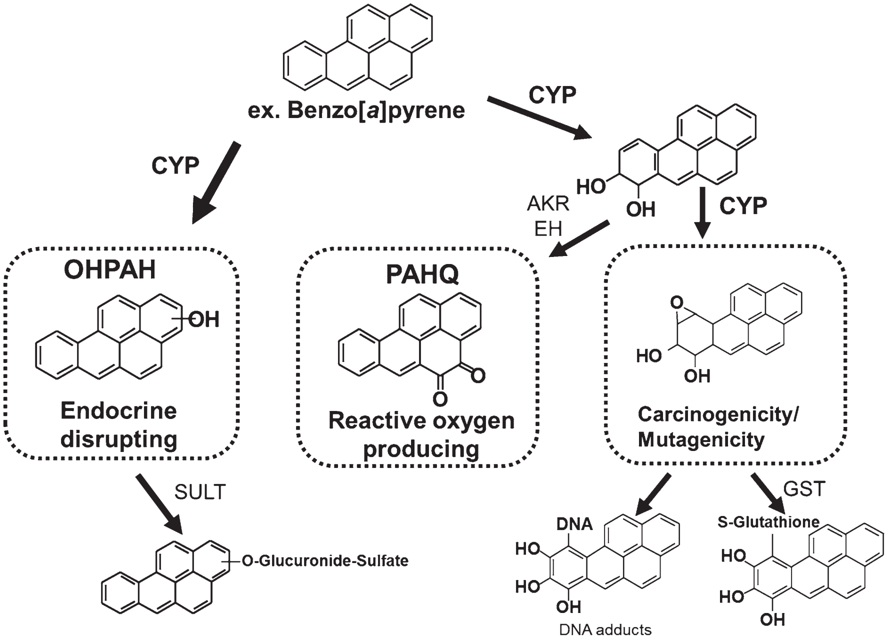

Fig. 17.1 Metabolic activation of PAHs. *AKR* aldo-keto reductase, *EH* epoxide hydrolase, *SULT* sulfotransferase, *GST* glutathione S-transferase

ligand-activated transcription factors – expressed especially in the liver, adipose tissue, and bronchial epithelial cells (Tsay et al. 2013) and are a basic helix/loop/helix (bHLH)- and Per/Arnt/Sim (PAS)-containing transcription factor (Denison et al. 2002). In its inactivated state, AhR forms a complex with heat-shock protein HSP90 and X-associated protein 2 (Meyer et al. 1998) and a co-chaperone protein p23 (Kazlauskas et al. 1999). Once activated by PAHs, AhR dissociates from this complex, translocates into the nucleus, and forms the heterodimer with ARNT. This AhR/ARNT dimer is able to bind to the xenobiotic response elements (XREs) in the promoter/enhancer region of AhR-responsive genes (Tsay et al. 2013) including drug-metabolizing enzymes such as those in the cytochrome P450 (CYP) family (i.e., CYP1A1, CYP1A2, CYP1B1, etc.). These AhR-regulated genes play important roles in the metabolism of PAHs.

The mechanisms of PAH metabolism induced by drug-metabolizing enzymes are shown in Fig. 17.1. First, PAHs are metabolized by phase I drug-metabolizing enzymes such as the CYP family. This metabolism generates two types of PAH derivatives, phenols and diols. PAH diols are further metabolized by aldo-keto reductase (AKR) and epoxide hydrolase (EH), followed by the generation of PAH quinones (PAHQs). We have previously reported that hydroxylated PAH (OHPAHs) and PAH quinones cause endocrine disruption and oxidative stress (Hayakawa et al. 2007; Motoyama et al. 2009). In addition, it is speculated that these derivatives are related to various diseases induced by PAH exposure. PAH diols are also metabolized by the CYP family and produce PAH diol-epoxides which are strongly mutagenic and carcinogenic. Therefore, it is a concern as various biological effects are attributed to the metabolism of PAHs. After phase I metabolism, PAH derivatives are further conjugated by phase II enzymes to make them more polar and easily detoxified metabolites through UDP-glucuronosyltransferase (UGT) and sulfotransferase (SULT), and the diol-epoxide is conjugated with glutathione (GSH) by glutathione S-transferase (GST). These metabolites migrate into the urine or bile for elimination from the body.

17.2 Estrogenic/Antiestrogenic Activity of PAH Derivatives

Nishihara et al. (2000) investigated the estrogenic activities of 517 chemicals by using a yeast two-hybrid assay system based on the ligand-dependent interaction of the estrogen receptor (ER) and its co-activators. The common structure among the compounds showing estrogenic activities is a phenol group with a hydrophobic moiety at the para-position and the absence of a bulky group at the *ortho*-position. The estrogenic and antiestrogenic activities of PAH derivatives have been reported by a number of researchers. For instance, Hirose et al. (2001) tested 12 hydroxybenzo[*a*]pyrene (OHBaP) isomers (from 1- to 12-OHBaPs) using the ERα and ERβ competition binding assay of the yeast two-hybrid system and demonstrated that 1-, 2-, 3-, and 9-OHBaPs show estrogenic activity, while 8-OHBaP shows antiestrogenic activity. Ebright et al. (1986) also reported the different ER binding affinity among structural isomers of OHBaPs. These reports suggest a relationship between binding affinity to the receptor, physiological activities, and structural characteristics (e.g., functional group position).

In order to elucidate the structural activities of PAH derivatives in more detail, we further investigated estrogenic and antiestrogenic activities of OHPAHs and other kinds of PAH derivatives, such as PAHQs, having two to six rings by using the yeast two-hybrid assay system (Hayakawa et al. 2007, 2011). We found that several OHPAHs composed of four or five rings show strong estrogenic or antiestrogenic activity (Fig. 17.2) (Hayakawa et al. 2007), similar to data reported from other laboratories. In addition, we have reported for the first time that PAHQs composed of three to five rings show both agonist and antagonist effects on endocrine receptors. We also found that the estrogenic activities of OHPAHs depend on three physical parameters: length-to-breadth (L/B) ratios of the rectangular van der Waals plane surrounding each PAH molecule, the distance between the oxygen atom of the phenol group and the hydrogen atom located farthest from the phenol group (O-H distance), and the partial charge of the phenol group (Hayakawa et al. 2007). L/B ratios and O-H distances for PAH derivatives are plotted in Fig. 17.3. From the results of this analysis, we found that the parameters of estrogenic OHPAHs are similar to those of estradiol (E_2) and diethylstilbestrol (DES) and that compositional flexibility of estrogenic OHPAHs is much smaller than that of antiestrogenic OHPAHs. Furthermore, compounds having a strong affinity to ER, such as E_2 and DES, have two hydroxyl groups with the appropriate O-O distance (Fang et al. 2001). The L/B

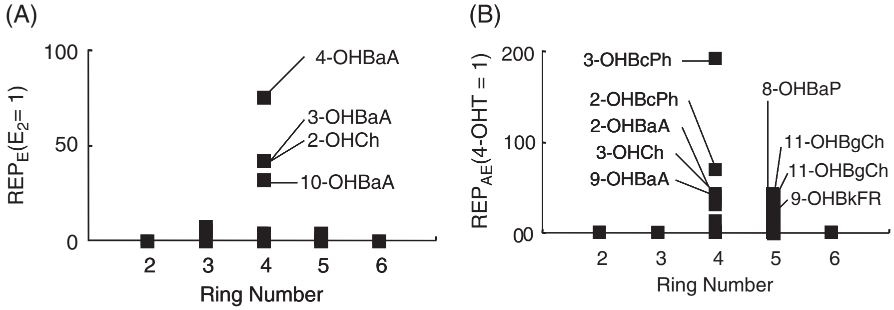

Fig. 17.2 Relationship between number of rings of OHPAHs and (**a**) REP$_E$ and (**b**) REP$_{AE}$ calculated from the values of E_2 and 4-OHT REP$_E$ and REP$_{AE}$ were calculated from the values of E_2 and 4-OHT (Reproduced from Hayakawa et al. (2007) with permission from the Journal of Health Science)

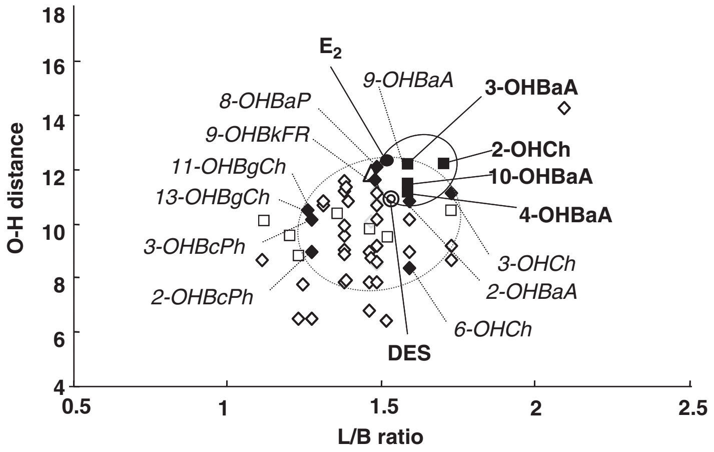

Fig. 17.3 Relationships between L/B ratio and O-H distance values of estrogenic and antiestrogenic OHPAHs. Human ERα was used in the assay. Symbols: ■; REPE >0.001, □; REPE <0.001, ◆; REPAE >0.1, ◇; REPAE <0.1, ⊚; DES, ●; E_2. In the case of E_2 and DES, O-O distance was used instead of O-H distance (Reproduced from Hayakawa et al. (2007) with permission from the Journal of Health Science)

ratios of E_2 and DES are 1.545 and 1.515, respectively. These L/B ratios and O-O distances are close to the values of L/B ratios and O-H distances of the OHPAHs in the small circle area in Fig. 17.3. The area of the L/B ratio and O-H distance of the strongly antiestrogenic OHPAHs is much larger than that of the strongly estrogenic OHPAHs. In the case of PAHQs, the L/B ratios of active PAHQs are in the range from 1.27 (BaP-1,6-Q) to 1.41 (BaP-7,10-Q) and in the range from 1.7 (1,4-ChQ) to 1.8 (1,2-ChQ) (Fig. 17.4). On the other hand, the O-H distances of estrogenic/antiestrogenic PAHQs are in the range from 8.2 Å (5,6-ChQ) to 11.5 Å (1,2-ChQ).

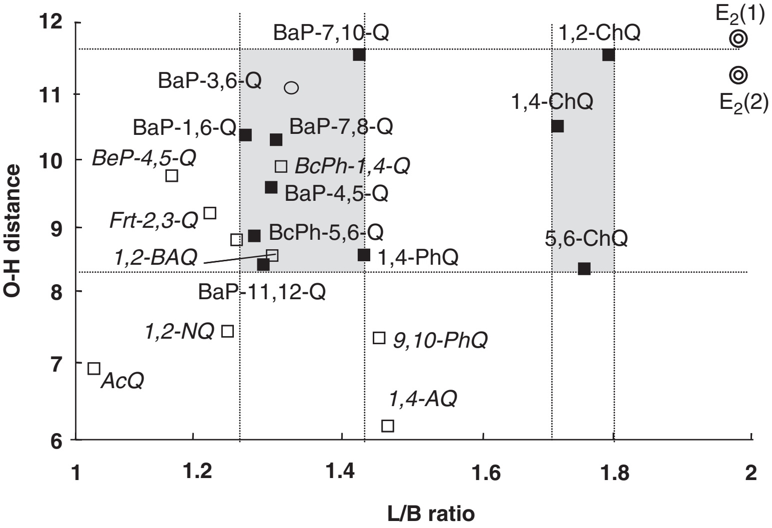

Fig. 17.4 Relationship between L/B ratio and O-H distance of estrogenic/antiestrogenic PAHQs. ■, antiestrogenic; ○, estrogenic; □, inactive (Reproduced from Hayakawa et al. (2011) with permission from the Journal of Health Science)

This range is close to the values of O-H distances of E_2 (11.7 Å and 11.2 Å). The values of inactive PAHQs are outside these areas with two exceptions, 1,2-BAQ and BcPh-1,4-Q. These results suggest that the estrogenic and antiestrogenic activities depend mainly on the position of the substituted groups rather than on the kinds of functional groups (Hayakawa et al. 2011) and that the activity of OHPAHs and PAHQs could be roughly predicted from their physical parameters.

17.3 *Ortho*-Quinoid Polycyclic Aromatic Hydrocarbons Induce Strong Oxidative Stress

The toxicities of PAHQs have been extensively studied, and several reviews are available (O'Brien 1991; Jarabal et al. 1998; Kumagai et al. 1998, 2000; Penning et al. 1999). PAHQs produce reactive oxygen species (ROS) such as the superoxide anion radical and hydrogen peroxide through redox cycling, and these induce oxidative stress (Lintelmann et al. 2005; Xia et al. 2006). For example, it has been demonstrated that *ortho*-PAHQs, such as 9,10-phenanthrenequinone (9,10-PQ), can catalyze the transfer of electrons from dithiol to oxygen, generating superoxide anion radicals. In order to obtain more information about the relationship between oxidative stress effects and structural characteristics of PAHQs, we evaluated the oxidative stress potential of various PAHQs having two to four rings, which have

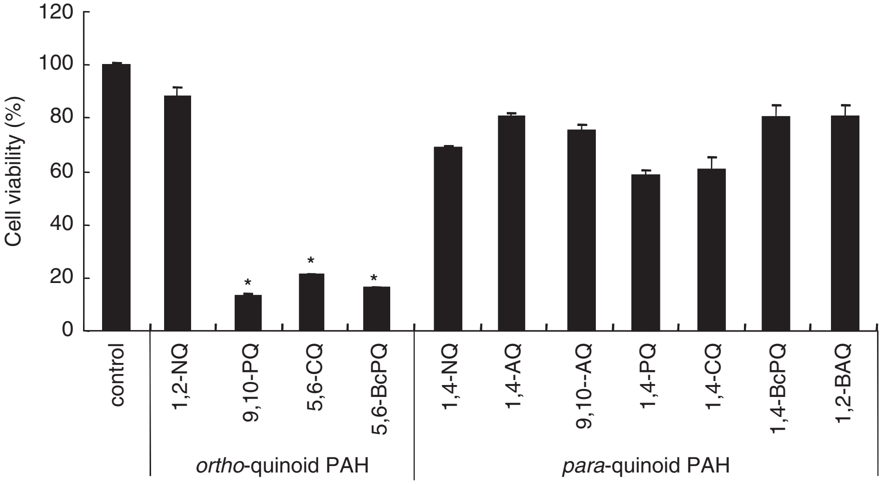

Fig. 17.5 Effects of PAHQs on the cell viability. A549 cells were incubated with 10 µM quinoid PAH for 12 h. The viability of the cells was determined by MTT assay. Each value is the mean ± SD of three determinations. Statistical significance, *: $P < 0.001$ vs. control (Reproduced from Motoyama et al. (2009) with permission from the Journal of Health Science)

been reported to exist in the atmosphere (Motoyama et al. 2009). To this end, we measured thiol consumption as an index for ROS generation of PAHQs and showed that *ortho*-PAHQs (9,10-PQ, 5,6-chrysenequinone (5,6-CQ), and benzo[*a*]pyrene-5,6-quinone (B[*a*]P-5,6-Q)) consume many more thiol groups when compared with *para*-PAHQs (1,4-naphthoquinone (1,4-NQ), 9,10-anthraquinone (9,10-AQ), 1,4-anthraquinone (1,4-AQ), 1,4-phenanthrenequinone (1,4-PQ), 1,2-benzoanthraquinone (1,2-BAQ), 1,4-chrysenequinone (1,4-CQ), and benzo[*c*]phenanthrene-1,4-quinone (B[*c*]P-1,4-Q)). Furthermore, we obtained the same results in experiments measuring cell viability as an index for PAHQ toxicity (Fig. 17.5). Together, this data strongly suggests that there is a structural activity relationship under which *ortho*-PAHQs have a stronger potential for ROS generation than *para*-PAHQs, and such a structural activity relationship might be related to the pulmonary dysfunction such as chronic inflammatory processes and acute symptomatic responses in the respiratory tract (Cho et al. 2004; Turuda et al. 2001; Tao et al. 2003; Lin et al. 2005). Several *ortho*-PAHQs, such as 9,10-PQ and 9,10-AQ, have been reported in the atmosphere at a concentration range from 20 to 730 pg m^{-3} (Bolton et al. 2000; Cho et al. 2004; Chung 2007). However, there is little information about the concentration ratios of *ortho*-type to *para*-type PAHQs in the atmosphere. Therefore, it is necessary to elucidate the amount of total PAHQs and the ratio of *ortho*-PAHQs in the atmosphere.

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Chapter 18
Carcinogenicity/Mutagenicity

Daisuke Nakajima and Mayuko Yagishita

Abstract Polycyclic aromatic hydrocarbons (PAHs) are known to possess toxicity leading to carcinogenesis (such as initiation and promotion activities). The International Agency for Research on Cancer (IARC) has classified and announced the results of its assessment of the carcinogenicity of each PAH. Indices such as toxicity equivalence factor (TEF), potency equivalence factor (PEF), and relative potency factor (RPF) have been proposed to express the potential of each PAH to cause cancer. Meanwhile, the initiation and promotion activities of extracts from airborne particulate matter have been measured directly and reported. The contribution of B[a]P to those activities is not always high, suggesting that PAHs other than B[a]P, or substances other than polycyclic aromatic compounds (PACs), are contributing to the carcinogenicity of the atmosphere.

Keywords IARC · Toxicity equivalency factor · Ames test (preincubation method, micro-suspension method) · Bhas assay

18.1 Carcinogenicity Classifications of PACs

Many polycyclic aromatic hydrocarbons (PAHs) are carcinogenic or mutagenic. Since Cook et al. (1933) separated benzo[a]pyrene (BaP) from coal tar, which was proven by Yamagiwa and Ichikawa (1915) to be carcinogenic, the carcinogenicity and mutagenicity of various PAHs have been examined and clarified. The International Agency for Research on Cancer (IARC) has assessed the carcinogenicity of chemical substances and their mixtures and compiled a list which includes PAH-related substances. Table 18.1 is an excerpt from the list of classifications by the IARC, showing PAH-related substances only (IARC 2016). For example, BaP

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Table 18.1 Agents classified by the IARC monographs

Group	CAS no.	Agent	Volume	Year
1	50-32-8	Benzo[*a*]pyrene	Sup 7, 92, 100F	2012
		Engine exhaust, diesel	46, 105	2013
		Outdoor air pollution, particulate matter	109	2016
		Tobacco smoke, secondhand	83, 100E	2012
		Tobacco smoking	83, 100E	2012
		Tobacco, smokeless	Sup 7, 89, 100E	2012
2A	53-70-3	Dibenz[*a,h*]anthracene	Sup 7, 92	2010
	191-30-0	Dibenzo[*a,l*]pyrene	Sup 7, 92	2010
	224-42-0	Dibenz[*a,j*]acridine	32, Sup 7, 103	2013
	5522-43-0	1-Nitropyrene	Sup 7, 46, 105	2014
	7496-02-8	6-Nitrochrysene	Sup 7, 46, 105	2014
	27208-37-3	Cyclopenta[*cd*]pyrene	Sup 7, 92	2010
2B	56-55-3	Benz[*a*]anthracene	92, Sup 7	2010
	91-20-3	Naphthalene	82	2002
	189-55-9	Dibenzo[*a,i*]pyrene	92	2010
	189-64-0	Dibenzo[*a,h*]pyrene	Sup 7, 92	2010
	193-39-5	Indeno[1,2,3-*cd*]pyrene	Sup 7, 92	2010
	195-19-7	Benzo[*c*]phenanthrene	92, Sup 7	2010
	202-33-5	Benz[*j*]aceanthrylene	92	2010
	205-82-3	Benzo[*j*]fluoranthene	92	2010
	205-99-2	Benzo[*b*]fluoranthene	92	2010
	207-08-9	Benzo[*k*]fluoranthene	92	2010
	218-01-9	Chrysene	92	2010
	224-53-3	Dibenz[*c,h*]acridine	103	2013
	226-36-8	Dibenz[*a,h*]acridine	32, Sup 7, 103	2013
	271-89-6	Benzofuran	63	1995
	602-87-9	5-Nitroacenaphthene	16, Sup 7	1987
	607-57-8	2-Nitrofluorene	46, 105	2013
	3697-24-3	5-Methylchrysene	Sup 7, 92	2010
	17117-34-9	3-Nitrobenzanthrone	105	2014
	42397-64-8	1,6-Dinitropyrene	46, 105	2013
	42397-65-9	1,8-Dinitropyrene	Sup 7, 46, 105	2013
	57835-92-4	4-Nitropyrene	46, 105	2013
	75321-20-9	1,3-Dinitropyrene	46, 105	2013
	105735-71-5	3,7-Dinitrofluoranthene	46, 65, 105	2013
		Diesel fuel, marine	45	1989
		Engine exhaust, gasoline	46, 105	2013
		Firefighter (as an occupational exposure)	98	2010
		Fuel oils, residual (heavy)	45	1989
		Gasoline	45	1989

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is classified into Group 1 (carcinogenic to humans); dibenz[a,h]anthracene and dibenzo[a,l]pyrene are in Group 2A (probably carcinogenic to humans); naphthalene, benz[a]anthracene (B[a]A), benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenzo[a,i]pyrene, and dibenzo[a,h]pyrene are in Group 2B (possibly carcinogenic to humans).

The carcinogenicity of nitroarenes (nitropolycyclic aromatic hydrocarbons) has also been assessed. For example, 1-nitropyrene and 6-nitrochrysene are classified into Group 2A, and 5-nitroacenaphthene, 2-nitrofluorene, 1,6-dinitropyrene, 1,8-dinitropyrene, and 1,3-dinitropyrene are classified in Group 2B.

Although PAHs are not necessarily a direct cause of cancer, mixtures known to contain PAHs, such as diesel exhaust, polluted outdoor air, and tobacco smoke, are also classified in Group 1. As described above, there is concern that PAHs generated by combustion may cause the development of cancer in humans.

18.2 Mutagenicity of PACs

PAHs are also known to function as carcinogenic initiators and promoters. The initiator activity of PAHs is known to damage DNA, causing subsequent mutations. The former activity is generally examined by in vitro tests such as the *umu* test, and the latter activity is assayed by the Ames test. The *umu* test involves measuring the amount of SOS recovery enzyme induced by DNA damage. The Ames test involves measuring the extent to which bacteria dependent on specific amino acids mutate back into independent ones (back mutation) due to exposure to chemical substances, thereby examining the degree of carcinogenic potential. Since these in vitro tests are easier and quicker than mutagenicity tests requiring animal experiments, they have been widely used in assessing the mutagenicity of PAHs (Nohmi and Matsui 1991).

PAHs that do not have functional groups are promutagens and do not exhibit mutagenicity in general but exhibit mutagenicity after metabolic activation by cytochrome P450 (CYP) enzymes such as CYP1A1, CYP1A2, and CYP1B1. These CYP enzymes are induced as a result of the coupling of aryl hydrocarbon receptors (AhR) and PAHs. Since bacteria used for the Ames test (*Salmonella typhimurium* is generally used) do not synthesize CYP, promutagens are measured by adding rat hepatic microsomes to the test system.

Meanwhile, it has also been reported that DNA damage and mutagenicity do not necessarily correlate with carcinogenicity. DNA damage due to chemical substances is considered to initiate chemical carcinogenicity, and then cancerous changes may occur by being subjected to the action of the promoter. Since canceration is also related to the action of the immune system and furthermore epigenetic chemical canceration has also been reported, in vitro tests to examine DNA damage and mutagenicity are often regarded as screening tests for carcinogenicity.

18.3 Tumor Promotion Activity of PAHs

As described previously, the carcinogenic potential of PAHs includes initiator and promoter functions. The promoter potential of PAHs was reported by Asada et al. (2005) using the Bhas promotion assay (Bhas 42 cell transformation assay at the tumor promotion stage), which was developed by Ohmori et al. (2004) by using Bhas 42 cells established by Sasaki et al. (1988). The Bhas 42 cell transformation assay at the tumor promotion stage is an easy and quick assessment method capable of assessing not only tumor promotion activity but also tumor initiation activity in just 3 weeks (OECD 2016). Table 18.2 summarizes the activities of tumor initiation and tumor promotion activities of PAHs. Although the promotion activity of B[a]P is reported to be negative, those of benzo[e]pyrene (B[e]P) and benzo[g,h,i]perylene are reported to be positive. The initiator-promotion activities can be classified into categories such as positive-negative, negative-positive, and positive-positive, which are typically represented by B[a]P, B[e]P, B[a]A, and anthracene. Although the promotion activity is one of the major action mechanisms of the carcinogenic process, there are few results on the assessment of PACs, and therefore more research needs to be performed.

18.4 Indices Related to the Carcinogenicity of PACs (TEF, PEF, and RPF)

There are various indices describing the intensity of PAH carcinogenicity. To express the carcinogenicity of dioxin mixtures, the toxicity equivalency factor (TEF) is set for individual isomers and multiplied with each concentration, and the sum of the obtained values is expressed as the toxicity equivalency quantity (TEQ). Regarding PAHs as well, studies on obtaining TEF in the same manner and using it to assess the risk of mixtures have been conducted. There are some examples where TEF is presented on animal testing data (Clement 1988; Chu and Chen 1984), and the values by Nisbet and LaGoy (1992) obtained by restudying those original data are used frequently (Table 18.3). Many other TEFs have been proposed (Sjogren et al. 1996; Collins et al. 1998; Malcolm and Dobson 1994; Kalberlah et al. 1995, McClure and Schoeny 1995). However, if there is no list containing the necessary TEF of PAHs to calculate TEQ from PAHs measured in the atmosphere, some of the proposed TEF and potency equivalency factor (PEF) values may be compared carefully and used in combination (Tsai et al. 2004). In another report, genotoxic equivalent factor was calculated based on the data of the H2AX assay (Audebert et al. 2012).

The Environmental Protection Agency (EPA) has started a detailed review to propose relative potency factor (RPF) of PAHs (US EPA 2010) and made draft proposals for the RPF of 26 PAHs. Assuming the RPF of BaP to be 1, RPF values more than ten times higher have been proposed for some substances: 20 for

Table 18.2 Summary of Bhas initiation and promotion assays

Chemical		IARC classification	Bhas 42 assay		Ames test			
					Frameshift mutation		Missense mutation	
			Initiation assay	Promotion assay	S9 (−)	S9 (+)	S9 (−)	S9 (+)
Group I	Benzo[*a*]pyrene	1	−	+	−	+		+
Group II	Benzo[*e*]pyrene	3	−	+	−	+	−	−
	Benzo[*g*,*h*,*i*]perylene	3	−	+	−	+		
	1-Nitropyrene	2A	−	+	I	I		
	Pyrene	3	−	+	−	+	−	I
Group III	Benz[*a*]anthracene	2B	+	+		+		
	Benz[*b*]anthracene		+	+	−	+	−	−
	Chrysene	2B	+	+	−	+		
	Perylene	3	+	+	−	+		+
Group IV	Acenaphthylene		−	±				
	Anthracene	3	−	−	−	+	−	−
	Coronene	3	−	±	−	+		
	9,10-Dipenylanthracene		−	±				
	Naphthalene	2B	−	−	−	−	−	−
	Phenanthrene	3	−	−	−	−	−	−

Excerpted from the table by Asada et al. (2005) and modified into the IARC classification at present
+ positive result, − negative result, ± equivocal result, *I* inconclusive result

Table 18.3 Toxicity equivalency factors (TEFs) for individual PAHs by Nisbet and LaGoy (1992)

Compound	TEF
Dibenz[*a,h*]anthracene	5[a]
Benzo[*a*]pyrene	1
Benz[*a*]anthracene	0.1
Benzo[*b*]fluoranthene	0.1
Benzo[*k*]fluoranthene	0.1
Indeno[1,2,3-*cd*]pyrene	0.1
Anthracene	0.01
Benzo[*g,h,i*]perylene	0.01
Chrysene	0.01
Acenaphthene	0.001
Acenaphthylene	0.001
Fluoranthene	0.001
Fluorene	0.001
2-Methylnaphthalene	0.001
Naphthalene	0.001
Phenanthrene	0.001
Pyrene	0.001

[a] A TEF of 1 appears to be appropriate for high doses of DBA, but the TEF of 5 is considered more likely to be applicable to environmental exposures (chemical-related tumor incidence rate of less than about 25%)

benzo[*c*]fluorene (BcFE), 60 for benz[*j*]aceanthrylene, 10 for dibenz[*a,h*]anthracene, 30 for dibenzo[*a,l*]pyrene, etc. There are only a few reports on the concentrations of these PAHs in the environment, and measurement data are still necessary to assess the health risk. Of these substances, actual measurements of the environmental concentration of benz[*j*]aceanthrylene, whose RPF is calculated to be 60, are desired, but it is difficult to obtain the standard substance. Actual measurement is difficult because of the difficulty in chromatographic separation of benzo[*j*]aceanthrylene from benz[*e*]aceanthrylene (RPF = 0.8). A separation technology and discriminating determination method need to be developed.

18.5 Mutagenicity of Semi-volatile Substances in the Atmosphere

Of the PAHs whose RPF is being studied by the EPA, one particular substance worth noting is BcFE, whose RPF is estimated to be 20. Of the PAHs in the atmosphere, BaP, which is pentacyclic and refractory, has been considered to contribute largely to carcinogenic risk. Meanwhile, BcFE, which is tetracyclic, may exist in relatively high concentrations in the vapor phase in East Asia in summer. Yagishita et al. (2015) sampled total suspended particulate (TSP) and semi-volatile PAHs in the summer and winter at 11 locations in Japan by using high-volume air samplers to which polyurethane foam (PUF) was attached, measured their concentration, and reported that the risk of BcFE might be five to seven times higher than that of BaP. Going forward, when assessing the carcinogenic risk due to atmospheric PAHs, semi-volatile components may require greater consideration.

There are few reports on the mutagenicity of semi-volatile substances in the atmosphere. A comparison between the mutagenicity of dust and that of semi-volatile substances performed by using PUF revealed that filter extracts exhibited higher activity in winter than summer and PUF extracts tended to exhibit higher activity in summer (Nakajima et al. 2008), which is why a detailed review is needed.

18.6 Mutagenicity of Total Suspended Particulate (TSP) in the Atmosphere in Japan and the Degree of B[*a*]P Contribution

Regarding the initiator activity of TSP in the atmosphere in Japan, mutagenicity was measured in Tokyo using the Ames test (micro-suspension method; Endo et al. 2016). For the period of 20 years from 1980 to 2000, approximately 60 specimens were collected annually using a high-volume air sampler, and measurements were made in each season. The mutagenicity of dust in Tokyo has decreased, and when metabolic activation using S9 mix was not performed, the frame-shift-type TA98 strain exhibited higher values than the base-pair substitution-type TA100 strain. Meanwhile, when metabolic activation was performed, the TA98 strain tended to exhibit higher values in the 1980s, whereas in the 1990s and later, the TA100 strain tended to exhibit higher values (Fig. 18.1), which indicates the change in composition that causes mutation. It is also reported that seasonal changes are smaller in the 1990s and occur later than in the 1980s.

The concentrations of six types of PAHs in the same sample were also reported (Ezoe et al. 2004), clarifying that PAH concentrations have decreased similarly. Nakajima et al. (2010) measured the mutagenicity of dust in the atmosphere (measured by the micro-suspension method, a modification of the Ames method) and PAH concentrations in summer and winter for 2 years at 11 locations in Japan. The values tended to be higher in the Tokyo metropolitan area and lower in the countryside, but the tendency of functional mechanisms was the same as the result of trend measurements performed in Tokyo previously. CYP generally metabolizes B[a]P into an epoxy form and induces base-pair substitution-type mutation (Shou et al. 1996). Nakajima et al. (2010) used the micro-suspension method and found that the contribution of B[a]P to the mutagenicity of dust in the atmosphere in Japan is less than 1% at most. This suggests that there are PAHs other than B[a]P that contribute largely to mutation. Detailed research of the contribution of nitroarenes and other toxic derivatives is needed.

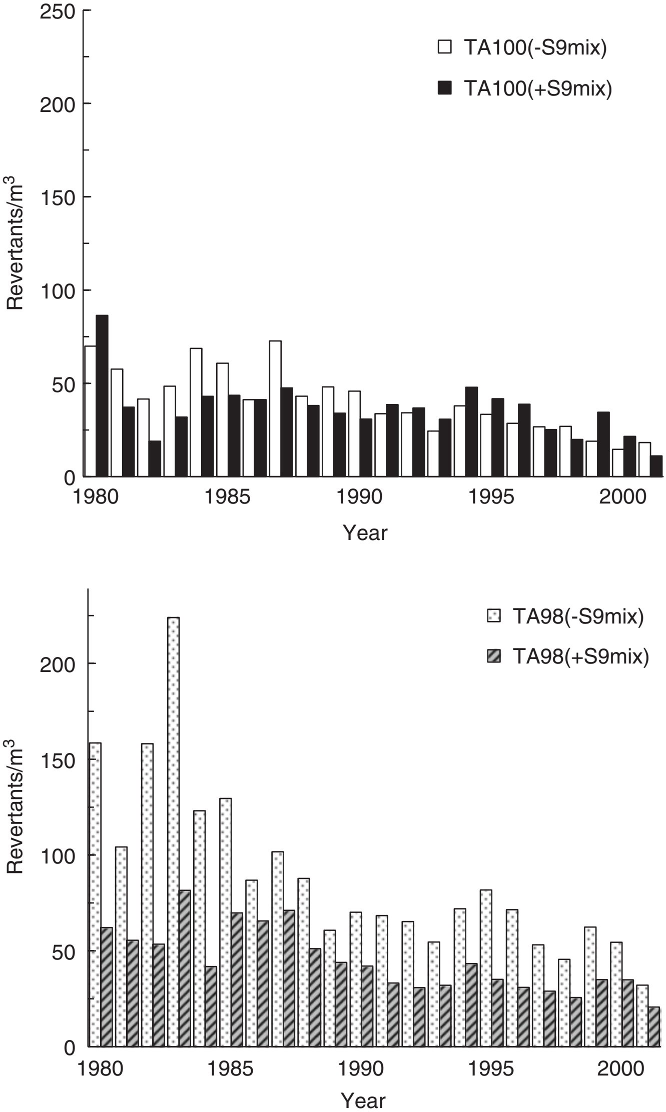

Fig. 18.1 Annual variation in TSP mutagenic activity per volume of ambient air in Tokyo from 1980 to 2001 for strains TA100 and TA98 (Modified from Endo et al. 2016)

Meanwhile, Ohmori et al. (2013) reported on the promotion activity of the atmospheric dust, taking samples at ten locations in Japan. Although the concentration of dust in the atmosphere tended to be higher in suburban areas such as Gunma, Ibaraki, Tokyo, and Kanagawa, the activity per unit air volume was higher in Hokkaido (Sapporo) in the winter. The activity per unit weight of dust exhibited a similar tendency. The activity by weight of dust, in particular, was reported to be more than two times higher in winter than summer at most locations. No activity was confirmed with the semi-volatile components collected by connecting PUF to the latter stage of the filter of the high-volume air sampler at any of the locations. Since there are only a limited number of reports on the tumor promotion activity of air samples, continuous compilation of data is desirable; a high-throughput in vitro bioassay such as Bhas 42 cell transformation assay at the tumor promotion stage would be useful for this purpose. The contribution of PAHs to the promoter activity in the atmosphere must also be studied.

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Chapter 19
Toxicities of Polycyclic Aromatic Hydrocarbons in Fish and Marine Invertebrates

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Abstract The toxicity of polycyclic aromatic hydrocarbons (PAHs) in aquatic animals is discussed, with particular focus on fish. In aquatic animals, our research group has recently investigated the toxicity of monohydroxylated PAHs (OHPAHs) which are metabolites of PAHs. In in vivo experiments on aquatic animals such as fish and sea urchin, it has been reported that OHPAHs are produced as metabolites from parent PAHs. In fish and sea urchin, OHPAHs exert greater toxicity than PAHs. Furthermore, to analyze the toxicity of PAHs on bone metabolism, we developed an original in vitro bioassay with fish scales having osteoblasts (bone formation cells) and osteoclasts (bone resorption cells). The sensitivity of our bioassay is quite high. In the case of cadmium, its concentration (even at 1×10^{-13} M) influenced osteoclastic activity in fish scales. Using a newly developed bioassay, it was demonstrated that seawater polluted with highly concentrated PAHs inhibited osteoblastic activity

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even if polluted seawater was added into a culture medium at a 500-fold dilution. Therefore, the prevention of PAH pollution is particularly important, given the toxicity of PAHs to aquatic animals.

Keywords Monohydroxylated polycyclic aromatic hydrocarbons · Aquatic animals · Bioassay · Fish scales · Sea urchins

19.1 Introduction

PAHs are widespread environmental contaminants derived from petroleum and generated through the incomplete combustion of fossilfuels, wood, and other organic materials (Lima et al. 2003). In the aquatic environment, PAH contamination occurs through storm water runoff, though atmospheric deposition of PAHs is now the largest source of aquatic PAH contamination (Lima et al. 2003; Li and Daler 2004). Furthermore, oil tankers are another anthropogenic source of PAHs, and oil spills are correlated with the major shipping routes in marine environments (Brekke and Solberg 2005). Moreover, accidental oil spills, such as those from the Deepwater Horizon, the Exxon Valdez, and the Nakhodka, have caused direct PAH pollution in the marine environment (Bue et al. 1998; Heintz et al. 2000; Hayakawa et al. 2006; de Soysa et al. 2012). PAH contamination is thus prevalent throughout the global marine system and directly affects marine organisms (Suzuki et al. 2016a). Here, we describe the toxicity of PAHs and their metabolites in aquatic animals, with the primary focus on fish.

19.2 Toxicity of PAHs in Fish

19.2.1 Carcinogenic Properties of PAHs

Some PAHs have been studied because of their cytotoxic, mutagenic, and carcinogenic properties (Verma et al. 2012). Eight PAHs typically considered to be possible carcinogens are benz[*a*]anthracene (BaA), chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene, indeno[*1,2,3-cd*]pyrene, and benzo[*g,h,i*]perylene (Menzie et al. 1992). In particular, BaP has been identified as being highly carcinogenic (Kuo et al. 1998; Wang et al. 2002). As BaP occurs in amounts of 20–40 ng per cigarette (Rodgman et al. 2000), the molecular evidence of the link between mutations caused by BaP and lung cancer has been investigated. Denissenko et al. (1996) reported that 60% of lung cancer cases were due to mutations caused by BaP and a few other PAHs. In addition, it has been known that BaP induces several carcinogenic responses in the cervix, bladder, breast, and prostate (Verma et al. 2012). Thus, in mammals, including humans, researchers have paid attention to the carcinogenicity of PAHs, but little research has focused on the adverse toxicity on marine organisms.

Epizootic neoplasia in fish is strongly associated with environmental chemical contamination, which has increased exponentially since the 1940s with the growth of synthetic organic chemical-producing industries (Bunton 1996). In several kinds of fish, epizootic events on hepatic and skin neoplasia are induced by the carcinogenic properties of PAHs, as seen in rodent animal models, suggesting that bioassays using fish can be applied to human health (Bunton 1996). An embryo-larval bioassay using fish has been adopted in the Organization for Economic Co-operation and Development (OECD) guidelines.

19.2.2 Toxicity of PAHs to Fish Embryogenesis

During fish embryogenesis, the heart is susceptible to toxic chemical contaminants in freshwater and marine habitats, and the disruption in cardiac function influences fish survival at all life stages (Incardona and Scholz 2016). This is important as the cardiovascular system is central to the extraction of atmospheric oxygen, specifically delivering oxygen to cell mitochondria and modulating cardiac output to meet the metabolic demands of active tissues (Farrell 1991). In fish and other vertebrates, swim performance is dependent on increases in cardiac output (Farrell 1991), indicating that the disruption of cardiac function by polluting chemicals is a major threat to fish. In crude oil from the Deepwater Horizon oil spill, which included three-ring PAH congeners (i.e., phenanthrene), the mechanism of embryonic heart failure was demonstrated through two pathways: (1) the inhibition of the inwardly rectifying potassium channel, which drives the repolarization of cardiac action potentials, and (2) a disruption of intracellular calcium cycling in cardiomyocytes, either by blocking the ryanodine receptor or the sarcoplasmic reticulum calcium pump (Brette et al. 2014).

In the early-life stage of fish, which are representative of aquatic animals, PAHs have been reported to cause bone deformities in freshwater fish such as zebrafish and medaka (Billiard et al. 2006; Farwell et al. 2006) as well as seawater fish such as Pacific herring and pink salmon (Barron et al. 2004). In an early-life stage in vivo bioassay using medaka, skeletal deformities were observed at around 1×10^{-7} M (Farwell et al. 2006). In an in vivo experiment regarding bone metabolism, sensitivity was fairly low because the effect of PAHs on osteoclasts and osteoblasts is indirect. A new in vitro assay that directly analyzes the influence of PAHs and their metabolites on both osteoclasts and osteoblasts of teleost species is needed.

19.2.3 Toxicity of PAHs on Immune Systems

The immune defense mechanisms of fish are similar to those for mammals, including cell- and humoral-mediated responses (Zelikoff 1998). Antibody-producing immune cells, similar to mammalian B-lymphocytes, are found in the spleen and kidneys of fish (Zelikoff 1998). T-lymphocytes with cell-mediated immunity are the primary cell type responsible for cell-mediated immunity in fish (Secombes et al. 2005). However, the effects of PAHs on the function of both B- and T-lymphocytes are contradictory and dependent on the dose and the compound tested in mammals (Smialowicz et al. 1997). In fish as well as in mammals, the effects of PAHs on specific immunity (both B- and T-lymphocyte functions) are not in agreement (Reynaud and Deschaux 2006).

In the case of nonspecific immunity, the toxicity of PAHs has been reported. Lysozymes are enzymes that act directly on the walls of Gram-positive bacteria and on the inner peptidoglycan layers of Gram-negative bacteria. When rainbow trout (*Oncorhynchus mykiss*) were injected with diesel-oil drilling mud, serum lysozyme levels were reduced at a dose of 0.6 ml kg/1 (Tahir and Secombes 1995). PAHs also influence fish phagocytes. In fish with livers contaminated with high concentrations of PAHs, chemotactic and phagocytic activities decreased (Weeks and Warinner 1986). Also, nonspecific cytotoxicity activity in mummichog (*Fundulus heteroclitus*) from the Elizabeth River, which was contaminated with PAHs, significantly decreased (Faisal et al. 1991). Thus, environmental pollutants influence fish immunity.

19.3 Endocrine-Disrupting Potential of OHPAHs

A common feature of the structure of estrogenic compounds is a phenol group with a hydrophobic moiety at the *para* position and the absence of a bulky group at the *ortho* position (Bekki et al. 2013). Therefore, the structural similarity of several OHPAHs to 17β-estradiol raises the possibility of strong estrogenic or antiestrogenic activities.

Using a yeast two-hybrid assay, Hayakawa et al. (2007) demonstrated that monohydroxylated polycyclic aromatic hydrocarbons (OHPAHs) bound to a human estrogen receptor (ER) while PAHs did not. Several OHPAHs with four aromatic rings, such as 3-hydroxybenz[*a*]anthracene (3-OHBaA), 4-hydroxybenz[*a*]anthracene (4-OHBaA), and 3-hydroxybenzo[*c*]phenanthrene (3-OHBcP), bound to human ER and showed estrogenic and antiestrogenic activity (Hayakawa et al. 2007). In rat cytosol as well, 2-hydroxybenz[*a*]anthracene bound strongly to ER (Ebright et al. 1986). In the ERα reporter assay using a human breast cancer cell line (MCF-7), 3-hydroxybenz[*a*]anthracene and 9-hydroxybenz[*a*]anthracene showed ERα binding activity too (Charles et al. 2000; Jaruchotikamol et al. 2007). In mammals, PAHs are converted into OHPAHs in the presence of cytochrome P4501A1 (Charles et al. 2000; Jaruchotikamol et al. 2007). In vivo, the endocrine disruption may be caused by OHPAHs but not by PAHs.

19.4 The Generation of OHPAHs in Fish

OHPAHs can be generated in animal bodies. After entering the body, PAHs bind to one of the nuclear receptors, the aryl hydrocarbon receptor (AhR), and then induce cytochrome P450 (CYP) drug-metabolizing enzymes such as CYP1A1, CYP1A2, and CYP1B1, which metabolize PAHs into various PAH derivatives, including OHPAHs (Bekki et al. 2013). In teleost species as well as in mammals, both AhR and CYP1A1 are present (Billiard et al. 2006; Brown et al. 2015). Therefore, PAHs may be converted into OHPAHs in the presence of cytochrome CYP1A1.

OHPAHs in the gall bladder of stargazers (*Xenocephalus elongates*) captured by fishermen in Toyama Bay were characterized. After acclimation for 3 days, these fish were anesthetized with ethyl 3-aminobenzoate, methanesulfonic acid salt (Sigma-Aldrich, Inc., St. Louis, MO, USA) and dissected. Bile was then collected with a syringe and was incubated with β-glucuronidase and arylsulfatase to remove glucuronic acid and sulfate. OHPAHs in the bile of stargazers were measured using gas chromatography with tandem mass spectrometry (GC-MS/MS) after trimethylsilyl derivatization with some modifications of the method of Wang et al. (2007). TMS-derivatized OHPAHs were separated on a DB5-MS capillary column coated with 5% phenylmethylpolysiloxane (60 m × 0.25 mm i.d., 0.25-μm film thickness: Agilent Technologies, Palo Alto, CA, USA). Almost all product ions of the analytes showed fragment ions $[M-31]^+$ and $[M-15]^+$ from the precursor ion ($[M]^+$). The concentration of OHPAHs was quantified using deuterated analytes as internal standards.

OHPAHs were detected in the bile of stargazers inhabiting the Toyama Bay. The results are shown in Fig. 19.1. As indicated, 1-hydroxynaphthalene (1-OHNap), 2-hydroxynaphthalene (2-OHNap), 2-hydroxyfluorene (2-OHFle), 2-hydroxyphenanthrene (2-OHPhe), 3-hydroxyphenanthrene (3-OHPhe), and 1-hydroxypyrene (1-OHPyr) were detected in the bile of stargazers. The most abundant compound in stargazers was 1-OHPyr. As teleost species are always exposed to PAHs, the conversion of PAHs into OHPAHs through CYP enzymes constitutes a threat to their health.

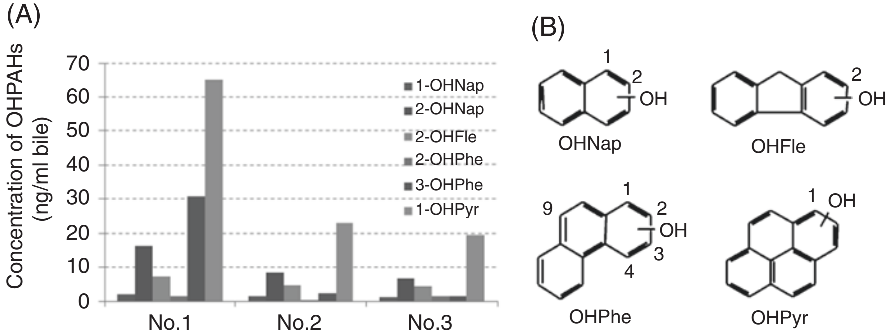

Fig. 19.1 The concentration of OHPAHs in the gall bladders of stargazers (*Xenocephalus elongates*)
(**a**) Concentration of each OHPAH in three stargazers; (**b**) chemical structure of the OHPAHs
1-hydroxynaphthalene: 1-OHNap; 2-hydroxynaphthalene: 2-OHNap; 2-hydroxyfluorene: 2-OHFle; 2-hydroxyphenanthrene: 2-OHPhe; 3-hydroxyphenanthrene: 3-OHPhe; 1-hydroxypyrene: 1-OHPyr

19.5 The Influence of OHPAHs on Fish Embryogenesis

The Japanese medaka (*Oryzias latipes*) is a model fish used in the OECD guidelines for the testing of chemicals. Using medaka embryos, we examined the toxicity of OHPAHs on embryogenesis (Chen et al. 2017).

As OHPAHs, especially 3-OHBcP, may have strong toxic effects on the endocrine system of vertebrates (Hayakawa et al. 2007), we examined the toxicity of 3-OHBcP on fish embryogenesis through an in ovo nanoinjection method. Nanoinjection uses a special glass micropipette to inject a nanolevel volume of liquid solution into a living cell under a microscope by using a micromanipulator. This method is widely known in transgenic experiments (Porazinski et al. 2010).

Nanoinjecting 3-OHBcP (1 nM) in ovo accelerated the development of medaka embryos on the first, fourth, and sixth days post fertilization (dpf). On the fifth dpf, the heart rates of embryos in the 1-nM 3-OHBcP exposure group were significantly higher than those in the control and solvent control groups (Chen et al. 2017). In addition, mRNA-Seq data analysis was performed to analyze in detail the mechanisms of these phenomena. Significant expression differences in 780 genes existed between the solvent control (four replicates) and the 3-OHBcP exposure (three replicates) groups. The results of mRNA-Seq analysis indicated that many genes related to heart development in exposed embryos significantly increased compared with those in control embryos. These results indicate that an abnormal development of the heart in the 3-OHBcP-exposed medaka embryo had occurred. Also, the expression of genes related to eye development (lens, beaded filament, and crystalline) increased due to 3-OHBcP exposure. Furthermore, the expression of genes related to muscle development, energy supply, and stress-response proteins significantly changed during early development in medaka. Thus, 3-OHBcP acts on several organs and is toxic to fish embryogenesis.

19.6 Fish Scales as a Suitable Model for the Analysis of Pollutants Including OHPAHs on Bone Metabolism

PAHs, such as BaP, were shown to inhibit osteogenesis in rat bone marrow cells (Andreou et al. 2004). BaP was also shown to inhibit osteoclastogenesis in mouse RAW264.7 macrophage cells, which differentiate into osteoclasts in the presence of the receptor activator of the NF-κB ligand (Voronov et al. 2008). In fish as well as mammals, bone deformities were reported in Pacific herring, pink salmon, and medaka in response to PAH exposure (Barron et al. 2004; Billiard et al. 2006; Farwell et al. 2006), suggesting that further research should be performed to understand the toxicity of PAHs to fish bone metabolism. However, the direct effect of PAHs and their metabolites on osteoclasts and osteoblasts has not been examined in fish because of the lack of a suitable assay system.

A teleost scale is a calcified tissue in which coexist osteoblasts (Fig. 19.2a), osteoclasts (Fig. 19.2b), and two layers of bone matrix—a bony layer, which is a thin, well-calcified external layer, and a fibrillary layer, which is a thick, partially calcified layer (Bereiter-Hahn and Zylberberg 1993; Yoshikubo et al. 2005; Suzuki et al. 2007; Ohira et al. 2007). The bone matrix, which includes type I collagen (Zylberberg et al. 1992), osteocalcin (Nishimoto et al. 1992), osteonectin, (Redruello et al. 2005), and hydroxyapatite (Onozato and Watabe 1979), is present in scales as well as in mammalian bone. Teleost scales have an important function in regulating blood calcium levels because teleost scales, which have both osteoblasts and osteoclasts, are known to function as potential internal calcium reservoirs similar to those in the endoskeletons of mammals (Suzuki et al. 2016b).

Using a functional calcium-regulating organ (teleost scales), we have developed a novel in vitro assay system (Suzuki et al. 2000, 2016b; Suzuki and Hattori 2002). This system can simultaneously detect the activities of both scale osteoblasts and

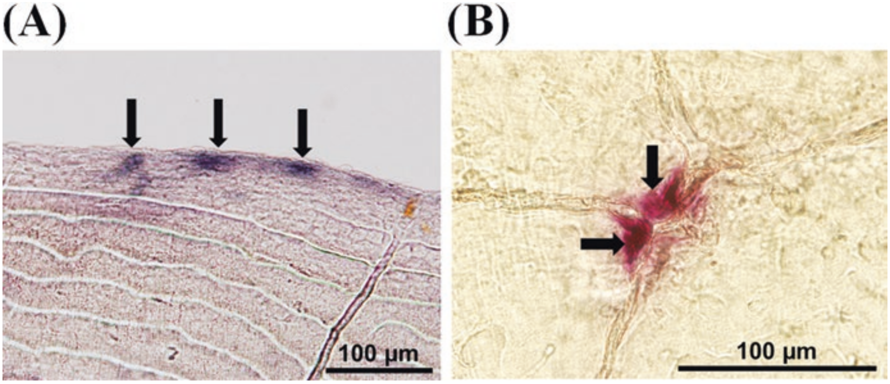

Fig. 19.2 Typical osteoblasts (**a**) and osteoclasts (**b**) in goldfish scales
(**a**) alkaline phosphatase staining for osteoblasts (arrows); (**b**) tartrate-resistant acid phosphatase staining for osteoclasts (arrows)

osteoclasts with alkaline phosphatase (ALP) and tartrate-resistant acid phosphatase (TRAP) as markers, as shown by the fact that in mammals, the effects of bioactive substances, such as hormones, on osteoclasts and osteoblasts have been investigated using ALP and TRAP as respective markers (Vaes 1988; Dimai et al. 1998; Suda et al. 1999). Using the scale assay system, we have demonstrated that calcemic hormones, such as parathyroid hormone (PTH) and calcitonin (CT), function in osteoblasts and osteoclasts. In the scales of goldfish, PTH, a hypercalcemic hormone, acts on osteoblasts and then stimulates osteoclastogenesis via receptor activators of nuclear factor-κB/receptor activators of the nuclear factor-κB ligand pathway, as PTH does in mammalian osteoblasts and osteoclasts (Suzuki et al. 2011). CT, which is well known as a hypocalcemic hormone, suppressed osteoclastic activity in the scales of goldfish, a freshwater teleost (Suzuki et al. 2000; Sekiguchi et al. 2007), and nibbler fish, a marine teleost (Suzuki et al. 2000). With the addition of calcemic hormones, our bioassay was sensitive to pollutants. In the case of cadmium, its concentration (even at 10^{-13} M) responded to osteoclasts in the scales of goldfish (Suzuki et al. 2004). Also, even 10^{-10} M tributyltin, a kind of marine environmental contaminant, significantly suppressed osteoblastic activity (Suzuki et al. 2006).

As described in section 1.3, OHPAHs with four aromatic rings, such as 3-OHBaA and 4-OHBaA, showed binding activity for human ER (Hayakawa et al. 2007). Thus, we examined the direct effect of OHPAHs (3-OHBaA and 4-OHBaA) on scale osteoclasts and osteoblasts in both goldfish and wrasse (a marine teleost) and compared them with 1-OHPyr as a negative control. To confirm the obtained results, the mRNA expressions of the cathepsin K (osteoclastic marker) and insulin-like growth factor-I (IGF-I; an osteoblastic marker) were examined in OHPAH-treated scales using reverse transcription-polymerase chain reaction (Suzuki et al. 2009). In goldfish, osteoclastic activity (TRAP activity) in the scales was significantly suppressed by 3-OHBaA and 4-OHBaA, although 1-OHPyr did not affect TRAP activity. Also, osteoblastic activity (ALP activity) decreased with both 3-OHBaA and 4-OHBaA and did not change with 1-OHPyr treatment. In wrasse as well as goldfish, both 3-OHBaA and 4-OHBaA suppressed TRAP and ALP activities. The marker mRNA expressions of both osteoclasts (cathepsin K) and osteoblasts (IGF-I) decreased in 4-OHBaA-treated scales as each TRAP and ALP activity did. Our data (Suzuki et al. 2009) are the first to demonstrate that in teleosts, OHPAHs—3-OHBaA and 4-OHBaA—inhibited both osteoclasts and osteoblasts and disrupted bone metabolism.

19.7 Influences of Seawater Highly Contaminated with PAHs on Fish Bone Metabolism

It has been reported that oil spills correlated very well with major shipping routes (Brekke and Solberg 2005). As described above, PAHs are toxic substances found in oil. Furthermore, spinal deformities were observed in fish inhabiting sea areas polluted by crude and heavy oil resulting from a tanker accident (de Soysa et al. 2012). However, worldwide, polluted areas exist even in the absence of shipping accidents.

The Suez Canal in Egypt links the Mediterranean Sea to the Red Sea. Since its inauguration in November 1869, many ships and oil tankers have used the canal. Furthermore, Alexandria, located at the mouth of the Nile, is an important port on the Mediterranean Sea route and fishing port with several kinds of marine resources. However, both crude oil and heavy oil are often included in the ballast water discarded by ships, and the marine pollution of the Mediterranean Sea coast and the Suez Canal worsens even if a shipping accident does not occur. It was found that the concentration of PAHs (approximately 1000 ng/l) in both the seawater of the Red Sea side of the Suez Canal and of the Alexandria port was remarkably high at around 100 times that of the sea of Japan (Suzuki et al. 2016a). Furthermore, this was demonstrated to be more likely caused by PAHs included in crude oil (Suzuki et al. 2016a). In an experiment, samples of polluted seawater were added into culture medium at dilution rates of 50, 100, and 500 and incubated with goldfish scales for 6 h. Thereafter, ALP and TRAP activities in the scales of goldfish were measured. Results showed that ALP activity in the scales was significantly suppressed by both polluted seawater samples, even if seawater was diluted up to 500 times, although TRAP activity did not change, at least in present conditions. In addition, the mRNA expressions of osteoblastic markers (ALP, osteocalcin, and the receptor activator of the NF-κB ligand) were significantly inhibited by polluted seawater, as was the ALP enzyme activity. Thus, we conclude that seawater polluted with highly concentrated PAHs influenced teleost bone metabolism.

19.8 The Presence of Cytochrome P450 Isoforms in Invertebrates

A great variety of invertebrates inhabit the marine environment. In scallops, phenanthrene (PHE) accumulated in their tissues after 96 h of exposure (200 µg/l). This accumulation in exposed scallops was 12.5-fold higher than that in control scallops (Piazza et al. 2016). In a Mediterranean mussel species (*Mytilus galloprovincialis*), the uptake rate of BaA exceeded depuration (Yakan et al. 2011), indicating that the bioaccumulation of PAHs is occurring in invertebrates. Furthermore, CYP isoforms were present (scallops, Piazza et al. 2016; polychaetes, Jørgensen et al. 2005; sea urchins, Goldstone et al. 2007; oysters, Pessatti et al. 2016). The mRNA expression of CYP isoforms in the mangrove oyster (*Crassostrea brasiliana*) increased 17~18-fold when placed in an area contaminated by PAHs such as naphthalene, phenanthrene, benzo[*a*]pyrene, and perylene (Pessatti et al. 2016). Also, after 96 h of phenanthrene (200 µg/l) exposure, the expression of the CYP isoform mRNA in the exposed scallops increased significantly, compared to control scallops (Piazza et al. 2016).

In invertebrates as well as fish, OHPAHs converted from PAHs may be toxic to invertebrates. However, the influence of OHPAHs on invertebrates has not been investigated.

19.9 Toxicity of PAHs and OHPAHs to Sea Urchins

We have examined the effect of both PAHs and OHPAHs on the embryogenesis of sea urchins (Suzuki et al. 2015). Adult sea urchins (*Hemicentrotus pulcherrimus*) were collected from the shore of the Toyama Bay side of the Noto Peninsula. Spawning was induced by the intracoelomic injection of 0.5 M KCl. Eggs and sperm from spawning animals were collected in 50-ml beakers containing filtered seawater (FSW). Prior to fertilization, the eggs were washed twice with FSW. Eggs used in the present study reached at least 95% fertilization within 10 min post-insemination. The eggs were divided into control and experimental groups. After fertilization, BaA and 4-OHBaA were added to seawater at concentrations of 10^{-8} and 10^{-7} M and kept at 18 °C while mixing lightly.

Embryos treated with BaA and 4-OHBaA were compared to control embryos. In the blastula and prism stages, there was no difference between the external features of the control and experimental groups. In the pluteus stage, morphological differences were observed. Spicule length (arrows in Fig. 19.3) was measured in embryos crushed by a cover glass. Spicule length was significantly inhibited by 4-OHBaA (10^{-8} and 10^{-7} M). BaA (10^{-7} M) suppressed the length of the spicule significantly, while the length did not change with BaA (10^{-8} M). The mRNA expression of the *Hemicentrotus pulcherrimus* spicule matrix protein 50 gene, which is a kind of spicule matrix protein, decreased significantly with 4-OHBaA treatment. *Hemicentrotus pulcherrimus* E26 transformation-specific gene 1 and *Hemicentrotus pulcherrimus* Aristaless-like homeobox gene 1, which are important transcription factors related to spicule formation, were significantly suppressed with 4-OHBaA. To determine the 4-OHBaA in BaA-treated embryos, embryos (pluteus stage) treated with BaA (10^{-7} M) were analyzed by high-performance liquid chromatography with fluorescence detection. As a result, 4-OHBaA (1.55 pmol) was detected in the BaA-treated embryos, although 4-OHBaA was not detected in the control embryos. We believe that OHPAHs converted from PAHs are toxic substances that inhibit early embryogenesis in sea urchins as well as in fish. This is the first investigation to demonstrate that OHPAHs suppress spicule formation in sea urchins.

19.10 Conclusions

In aquatic animals, we have discovered the toxicity of OHPAHs, metabolites of PAHs. Judging from the obtained data, the toxicity of OHPAHs is stronger than that of PAHs, at least in fish and sea urchins. Furthermore, to analyze the toxicity of

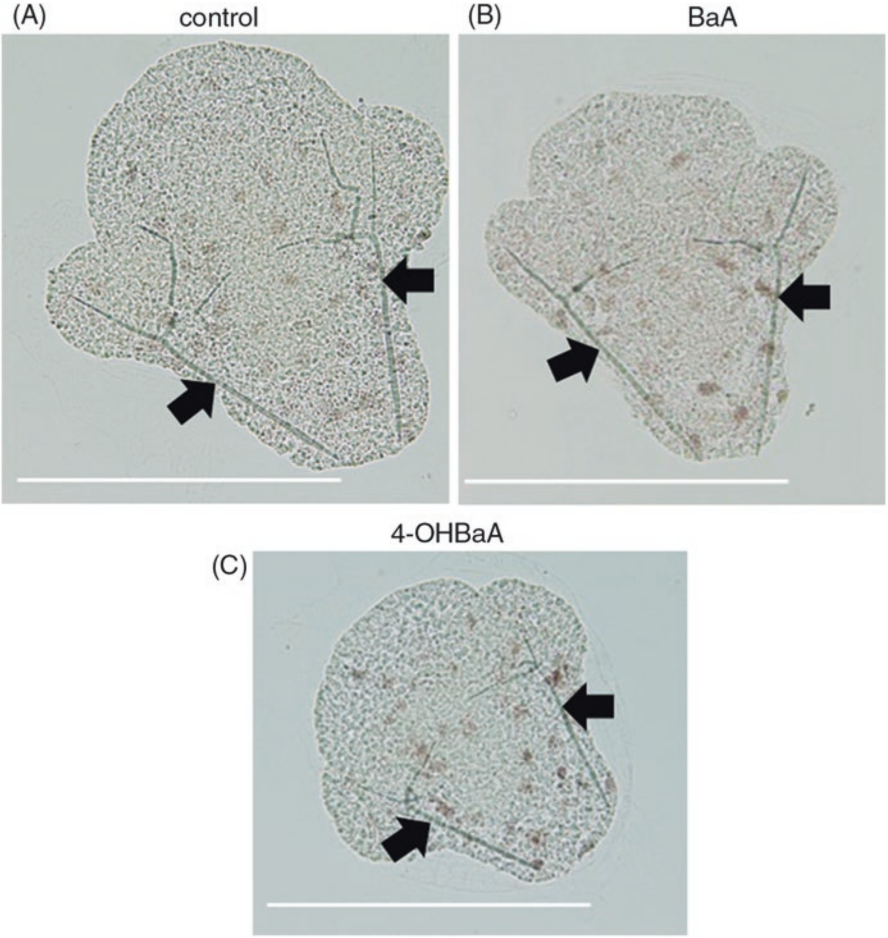

Fig. 19.3 Influences on spicule formation in control (**a**) benz[*a*]anthracene (BaA) (1 × 10^{-7} M) (**b**) and 4-hydroxybenz[*a*]anthracene (4-OHBaA) (1 × 10^{-7} M); (**c**) treated embryos. Spicule length (arrows) was measured using embryos crushed by a cover glass. Bar: 100 µm

PAHs and OHPAHs on bone metabolism, we developed an original in vitro bioassay with fish scales, which have osteoblasts (bone formation cells) and osteoclasts (bone resorption cells). Using our original bioassay, we discovered that seawater polluted with highly concentrated PAHs inhibited osteoblastic activity, even if polluted seawater was added into the culture medium at 500-fold dilution. OHPAHs, which occur with accumulated PAHs, may have toxic influences on aquatic animals, even if the PAH levels in the aquatic environments are low. Thus, we should emphasize the prevention of aquatic PAH pollution because of the toxicity of OHPAHs.

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Part VII

Environmental Standards and Guidelines

Chapter 20
Environmental Standards and Guidelines

Yayoi Inomata

Abstract This chapter describes the environmental standards for PAHs, especially benzo[a]pyrene (BaP), which are substances that increase the risk of cancer in humans. Although there is no environmental standard in the world, several criteria (such as target values, setting values, and reference levels) have been considered by several organizations and countries. These range from 0.1 to 2.5 ng m^{-3}. In the case of the World Health Organization (WHO) air quality guidelines, the reference level (0.12 ng m^{-3}) was estimated assuming WHO unit risk for lung cancer PAH mixtures and an acceptable risk of additional lifetime cancer risk of approximately 1×10^{-5}.

Results from a trend analysis of BaP show that the concentrations of BaP have decreased with seasonal variation with highs in the winter and lows in the summer in European Monitoring and Evaluation Programme (EMEP) regions as well as Japan. The reduction of [BaP] in the EMEP region during the period from 1990 to 2012 was 28%. However, [BaP] slightly increased (about 1%) in 2012. The annual reduction rate for each country in the EMEP region was subjected to large variability. In Japan, reductions in [BaP] between 2002 and 2012 was estimated at about 49%.

Keywords Environmental standards · BaP · Trend analysis · EMEP · Japan

20.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the primary environmental pollutants emitted from anthropogenic activities during the incomplete combustion of fossil fuels (i.e., coal, oil, petrol) and biomass such as wood. The weight of evidence from epidemiological studies for PAHs based on inhalation and occupational exposure suggests an increased risk of adverse health effects (i.e., carcinogenicity, genotoxicity) with lung cancer a predominant outcome (WHO 2003). In particular,

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benzo[a]pyrene (BaP) is recognized as carcinogenic in humans, based on animal experiments (IARC 2015) and therefore will be a particular focus of this chapter.

In this chapter, the criteria for evaluating and limiting the atmospheric PAH concentrations – as determined by several organizations and countries – are described and compared. The results of trend analyses of BaP concentrations in the European Monitoring and Evaluation Programme (EMEP) region and Japan are also described.

20.2 Comparison with the Various BaP Guidelines in the World

Environmental standards for PAHs have not been globally determined. However, several definitions for BaP environmental standards such as reference values, setting values, and target values are recommended by several organizations and countries. It is important to recognize that these assessments are prepared at different times, for different purposes, using different guidelines and methods. Table 20.1 shows the criteria for atmospheric PAH concentrations as established by several organizations and countries. A brief description of these criteria are described below.

20.2.1 World Health Organization (WHO)

The WHO has not set an air quality guideline value for atmospheric BaP concentrations for human health. However, the WHO set the target value as 1 ng m^{-3} based on lifetime cancer risk of approximately 1×10^{-4} (WHO 2003). These criteria were based on the unit risk (lifetime exposure to a mixture represented by 1 ngm^{-3} BaP) of 8.7×10^{-5} (ng m^{-3})$^{-1}$ for BaP. The unit risk was estimated as follows: Using a linearized multistage model, the most plausible lifetime unit risk estimate associated with a continuous exposure to 1 μgm^{-3} from coke oven emissions in ambient air was 6.2×10^{-4}. Using BaP as an indicator of PAH mixtures from coke oven emissions and similar combustion processes in air, 0.71% BaP was included in the benzene-soluble fraction of coke oven emissions, and a lifetime risk of respiratory cancer of 8.7×10^{-5} (ng m^{-3})$^{-1}$ was calculated.

The WHO has also set the reference level for BaP concentrations as 0.12 ng m^{-3}, which was estimated by assuming a WHO unit risk for lung cancer for PAH mixtures and an acceptable risk for additional lifetime risk of approximately 1×10^{-6}.

20.2.2 The European Union (EU)

The target value for mean annual BaP concentrations for minimizing human health risk is set at 1 ng m^{-3} (EEA 2016). Here the target value is a fixed concentration in the ambient air with the aim of avoiding, preventing, or reducing harmful effects on

Table 20.1 List of the criteria for BaP

Organization or Journal	Location	References	BaP	Environmental standards	Memo
European Environment Agency	EU	Air quality in Europe-2016 report	1 ng m^{-3}	EU target value (EU 2004)	
WHO			0.12 ng m^{-3}	WHO reference level (WHO 2013)	As the WHO has not set air quality guidelines for BaP, the reference level was estimated assuming WHO unit risk for cancer for PAH mixture and an acceptable risk of additional lifetime cancer risk of approximately 1 in 100,000 (ETC/ACM 2011)
MFE of New Zealand (2003)	NZ	New Zealand	0.3 ng m^{-3}	Environmental standard	
MEP of China (2012)	China	China	1 ng m^{-3}	Ambient air quality standard	
			1 ng m^{-3}	Annual	Class 1 special region such as national park; class 2 all other areas including urban and industrial areas
			2.5 ng m^{-3}	24HR	
The occupational safety and health administration (OSHA)	USA	ATSDR (2012)	0.2 mg m^{-3}	An 8-h time-weighted permissible exposure level	Workplace; a standard relating to PAH in the workplace (coal tar pitch volatiles and coke oven emissions)
			0.15 mg m^{-3}	Standard for coke oven emissions	Workplace
The National Institute for Occupational Safety and Health (NIOSH)	USA	ATSDR (2012)	0.1 mg m^{-3}	Coal tar pitch volatile agents	Workplace
American conference of governmental industrial hygienists	USA	ATSDR (2012)	0.2 mg m^{-3}	Threshold limit value for a normal 8-h workday and a 40-h workweek to which nearly all workers may be repeatedly exposed	Workplace

human health and the environment as a whole. Also, upper and lower assessment thresholds (0.6 and 0.4 ng m^{-3}, respectively) are established to assess ambient air quality. The reference level as an annual mean was estimated at 0.12 ng m^{-3}, assuming a WHO unit risk for lung cancer for PAH mixtures (WHO 2010) and an acceptable risk for additional lifetime cancer risk of approximately 1×10^{-5} (ETC/ACM 2011).

20.2.3 The US Environmental Protection Agency (US EPA)

The US Environmental Protection Agency (EPA) developed a potential equivalency factor (PEF) methodology to evaluate the toxicity and assess the risks of a mixture of structurally related chemicals with a common mechanism of action. A PEF is an estimate of the relative toxicity of a contaminant and assesses the risks for environmental mixtures of a chemical compared to a reference chemical, with BaP being used for carcinogenic PAHs (c-PAHs). Table 20.2 summarizes the PEFs for c-PAHs.

20.2.4 The Occupational Safety and Health Administration (OSHA)

The US Occupational Safety and Health Administration (OSHA) has set a permissible exposure level for PAHs in the workplace at 0.2 mg m^{-3} (Agency for Toxic Substances and Disease Registry (ATSDR) 2012). The OSHA does not set standards for a specific substance. The OSHA has mandated a permissible PAH exposure in a workroom over an 8-h time period at 0.2 mg m^{-3} based on measurement of the benzene-soluble fraction of coal tar pitch volatiles. The OSHA standard for coke oven emissions is 0.15 mg m^{-3}.

Table 20.2 Toxicity equivalency factors for carcinogenic polycyclic aromatic hydrocarbons

Compounds	TEF[a]	IARC class[b]	Inhalation unit risk (μg m^{-3})$^{-1}$
Benzo(*a*)pyrene	1	1	1.1E-03
Benz(*a*)anthracene	0.1	2B	1.1E-04
Benzo(*b*)fluoranthene	0.1	2B	1.1E-04
Benzo(*k*)fluoranthene	0.1	2B	1.1E-04
Chrysene	0.01	2B	1.1E-05
Dibenz(*a*,*h*)anthracene	1.1	2A	1.2E-03
Indeno(1,2,3-*c*,*d*)pyrene	0.1	2B	1.1E-04
Nitropyrene, 4-	0.1		1.1E-04

[a]USEPA (2013); [b]IARC (2015)

20.2.5 The National Institute for Occupational Safety and Health (NIOSH)

The National Institute for Occupational Safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products not exceed 0.1 mg m^{-3} for a 10-h workday, within a 40-h work week (ATSDOR 2012).

20.3 Trends in Atmospheric BaP Concentrations in Japan and EMEP

20.3.1 Trend Analysis Methods

In order to investigate the temporal variation of atmospheric BaP concentrations in Japan, statistical trend analyses are performed using a program prepared by EMEP/Meteorological Synthesizing Centre-East (MSC-E) (Shatalov et al. 2014). This analysis assumes that PAH air concentrations can be decomposed into three components: main, seasonal, and residual components.

The BaP concentrations (C_t) in the atmosphere at a certain time are calculated through a bi-exponential approximation. The concentrations consist of main (C_{main}), seasonal (C_{seas}), and residual (C_{res}) components:

$$C_t = C_{\mathrm{main}} + C_{\mathrm{seas}} + C_{\mathrm{res}}, \tag{20.1}$$

$$C_{\mathrm{main},t} = a_1 \exp\left(-t / T_1\right) + a_2 \exp\left(-t / T_2\right), \tag{20.2}$$

$$\begin{aligned} C_{\mathrm{seas},t} = {} & a_1 \exp\left(-t / T_1\right)\left(b_{1,1} \cos\left(2\pi t - \varphi_{1,1}\right) + b_{1,2} \cos\left(4\pi t - \varphi_{1,2}\right) + \cdots\right) \\ & + a_2 \exp\left(-t / T_2\right)\left(b_{2,1} \cos\left(2\pi t - \varphi_{2,1}\right) + b_{2,2} \cos\left(4\pi t - \varphi_{2,2}\right) + \cdots\right) \end{aligned} \tag{20.3}$$

$$C_{\mathrm{res},t} = C_t - C_{\mathrm{main},t} - C_{\mathrm{seas},t} \quad t = 0,2,3,\ldots,N \tag{20.4}$$

where a and b are coefficients and φ is the phase shift. These parameters are determined through the least squares method. T_1 and T_2 are time constants for rapid and slow decreased exponential function, and ($N + 1$) is the year of analytical period.

The trend analytical value, C_t in other words [BaP], is determined by the following:

$$C_t = C_{\mathrm{main}} + C_{\mathrm{seas}} \tag{20.5}$$

Total decreases during the analytical period and annual decreasing rates are calculated by using the value of C_{main}.

The decreasing rate during the analytical period (R_{tot}) and annual decreasing rate (R_{ave}) are estimated by the following equations:

$$R_{\text{tot}} = \left(C_{\text{beg}} - C_{\text{end}}\right) / C_{\text{beg}} = 1 - C_{\text{end}} / C_{\text{beg}} \tag{20.6}$$

$$R_{\text{ave}} = 1 - \left(C_{\text{end}} / C_{\text{beg}}\right)^{1/N} \tag{20.7}$$

where C_{beg} is the concentration at the beginning of analysis, C_{end} is the concentration at the end of analysis, and $(C_{\text{end}}/C_{\text{beg}})^{1/N}$ is the geometric mean of the decreasing rate.

The amplitudes of the normalized seasonal component for each year can be calculated as

$$A_i = \left(\max\left(C_{\text{seas},i} / C_{\text{main},i}\right) - \min\left(C_{\text{seas},i} / C_{\text{main},i}\right)\right) / 2 \tag{20.8}$$

where max and min are taken within a year i.

The parameter of residuals can be defined as

$$F_{\text{res}} = \sigma\left(C_{\text{res},i} / C_{\text{main},i}\right) \tag{20.9}$$

where σ stands for the standard deviation over the considered periods.

20.3.2 Trend Analysis of BaP in the EMEP Region

It was reported that BaP concentrations showed decreases at two thirds of the monitoring sites between 2007 and 2014 (EEA 2016). However, the EEA reported that exposure to BaP pollution is quite significant and widespread, in particular in central and eastern Europe. About 20–24% of the European urban population was exposed to BaP at annual mean concentrations above the European target value (1 ng m^{-3}) in 2014, and about 88–91% of the European urban population was exposed to BaP concentrations above the estimated reference level of 0.12 ng m^{-3} (EEA 2016). Values above 1 ng m^{-3} were measured at urban as well as suburban stations. In particular, values above 1 ng m^{-3} are most predominant in central and eastern Europe.

In the EMEP region, a trend analysis of BaP pollution was performed for the period between 1990 and 2012 (EMEP 2015, 2016). There was a reduction in [BaP], which means that the trend analytical value of BaP in the EMEP region is become to decrease 28% during the period. In particular, the maximum reduction occurred in the beginning of the analysis period. It was noted however that levels of [BaP] tended to increase (by about 1%) in 2012 with statistically significant changes at 90% confidence levels in most of EU28 and Eastern Europe, Caucasus, and Central Asia countries. [BaP] in most of the EMEP countries was also characterized by seasonal variation with high concentrations in the winter and low concentrations in the summer. [BaP] during the winter season exceeded the annual average value. The difference in the seasonal variation among these countries can be explained by their geographical location associated with meteorological conditions as well as emissions.

20.3.3 Trend Analysis of BaP in Japan

Under the purview of the Japanese Ministry of Environment, BaP concentrations are monitored in Japan. The number of monitoring sites varied between 297 and 366 during the period from 2000 to 2013. The monitoring sites were classified into three categories, residential, roadside, and industrial regions. The measurements of BaP were conducted over 24-h sampling periods monthly. Monthly average values of BaP concentrations for each category were used for the trend analysis. Details of this analysis are described in Inomata et al. (2016).

It was found that [BaP] concentrations in each category are characterized by a decreasing trend with clear seasonal variations with highs in autumn-winter and lows in summer seasons. The highest values were found in the industrial regions, followed by roadsides and residential regions. The amplitude of seasonal variation, which is large in winter and small in summer, also becomes smaller and was associated with decreasing [BaP]. The contribution of seasonal variation against [BaP] variation was 58% for residential, 31% for roadsides, and 50% for industrial regions. It is also noted that [BaP] in winter exceeded the annual average value several times. The reduction of [BaP] for the period between 2002 and 2012 was estimated at about 49% for residential regions, 40% for industrial regions, and 53% for roadsides. The maximum reduction occurred in the beginning of the period, and the reduction rate becomes smaller. The residual component, which means the variations not described by main and seasonal components, is 21% for residential regions, 29% for industrial regions, and 21% for roadsides. Larger residue components near the industrial region in comparison with those in residential and roadside regions suggest that BaP emission from the stationary industrial sources occurred throughout the year (Fig. 20.1).

Figure 20.2 shows the annual average [BaP] (residential, roadside, industrial regions) in Japan during the period from 2002 to 2012. The [BaP] in Japan for the three categories was less than the target value in EU (1 ng m^{-3}). However, [BaP] in the three categories did not satisfy the reference level (0.12 ng m^{-3}) set by the WHO air quality guidelines.

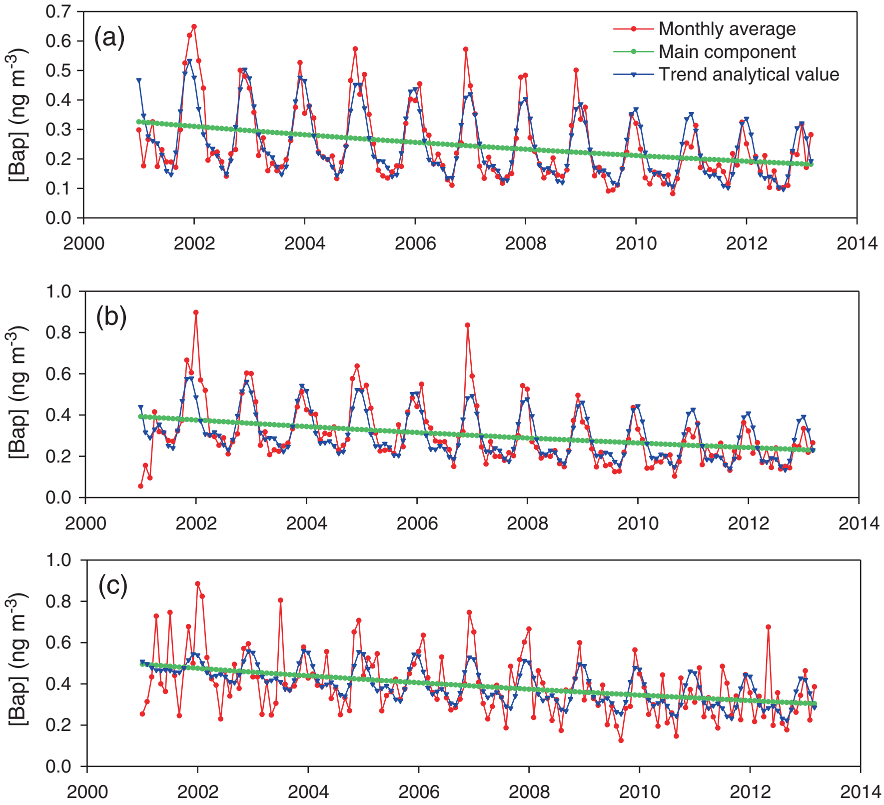

Fig. 20.1 Trend analysis of temporal variations of [BaP] in Japan. The red line corresponds to the monthly average observation value. The green line corresponds to the main component, and the blue line corresponds to the trend analytical value of [BaP]. (**a**) Residential, (**b**) roadside, (**c**) industrial regions

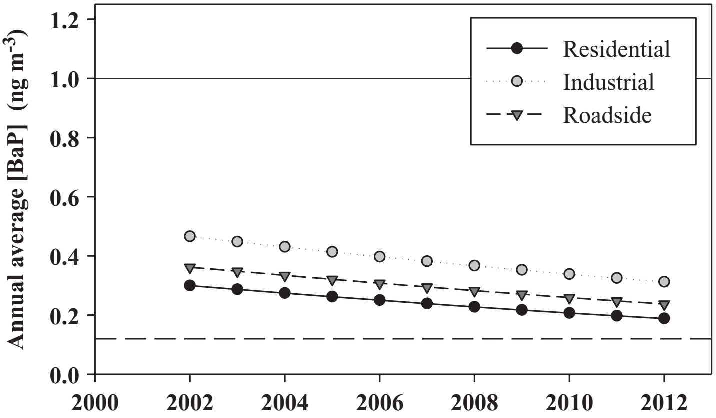

Fig. 20.2 Time variation of annual average [BaP] for three regions (residential, industrial, and roadside) in Japan. The horizontal line (1 ng m^{-3}) is the target value in the EU, and the dashed line (0.12 ng m^{-3}) is the reference level set by the WHO. As the WHO has not set air quality guidelines for BaP, the WHO reference level was estimated assuming an additional lifetime cancer risk of 1×10^{-5}

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