Polycyclic Aromatic Compounds in the Atmosphere – A Review Identifying Research Needs

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Most of the 16 EPA priority PAHs (or a subset of these) are targeted in the current monitoring of air and air pollution studies. However, other parent PAHs may account for up to another ≈10%, nitro-PAHs up to ≈20%, and oxy-PAHs for even more. The reactivity in the atmospheric gas and particulate phases is incompletely quantified, in particular with regard to coverage of aerosol matrix diversity and photochemical age. Therefore, the model-based characterization of exposure is still limited. Nitro- and oxy-PAHs pose a higher health risk in ambient air than parent PAHs but have not been measured as extensively so far and are usually not included in monitoring programs. Nitro-PAHs are also interesting as tracers for air pollution source identification and pathways of photochemistry. Among heterocyclic aromatic compounds in ambient air dibenzofuran and dibenzothiophene should be targeted.

Key Words: aerosol, air, heterocycles, nitro-PAHs, oxy-PAHs

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and their major transformation products (oxy-PAHs, nitro-PAHs, hydroxyl-PAHs) have been studied in ambient air as educts and products of photochemistry, as potentially harmful compounds for human health and vegetation (including crops) and because of their suitability for air pollution source identification and as tracers for atmospheric long-range transport. Among atmospheric trace chemical substances PAHs together with their photochemical products probably form the class
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most harmful to human health (1–4). Some PAHs, namely benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene, were found to bio-accumulate in the environment (5–7). Therefore, and because of resistance to degradation, these PAHs are discussed as POPs candidates, while the POPs Protocol (Aarhus Protocol) to the Convention on Long-range Trans-boundary Air Pollution (8) considers all PAHs to be POPs. Monitoring in the atmospheric environment mandated by international agreements and regimes is on-going in Europe, North America and the Arctic (8–12).

This article aims to identify polycyclic aromatic compounds studied in research and monitoring programs in the atmospheric environment and to identify research needs.

LEVELS AND DISTRIBUTION IN AMBIENT AIR

The distribution and fate of PAHs in the atmosphere has been the subject of numerous studies covering a wide range of spatio-temporal scales and relevant sources (13, 14). Most routine monitoring programs and air pollution studies have been targeting parent 2–6 ring PAHs, namely the 16 EPA priority PAHs (16 EPA PAHs, i.e., acenaphthene, acenaphthylene, fluorene, naphthalene, anthracene, fluoranthene, phenanthrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, pyrene, benzo[ghi]perylene, benzo[a]pyrene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]-pyrene) or a subset of these, e.g., the aforementioned four bio-accumulative PAHs, or benzo[a]pyrene only. The choice is often not scientifically based but results from the requirements of national regulation, available (accredited) methods and the common interest in this substance group. The concentration levels of the 16 EPA PAHs (total, i.e., sum of gaseous and particulate phase) observed in near-ground air are in the 1–400 ng m$^{-3}$ range in urban (15–17) and 0.1–3 ng m$^{-3}$ in remote continental environments (14, 18). Close to sources much higher concentration levels can be found in winter than in summer because of the seasonalities of the emissions (more combustion in winter, in particular residential heating) and photochemistry (stronger in summer). From marine environments 0.2–10 ng m$^{-3}$ and from the Arctic still 0.02–3 ng m$^{-3}$ were reported (14). However, apart from meridional long-range transport also local combustion sources may contribute to atmospheric pollution in the Arctic and may even have dominated for years on Svalbard (14, 19). For the Antarctic the analysis of several years of advection of air masses indicated that atmospheric PAH pollution was exclusively fed from sources within the region, i.e., ships and research stations (20). Similar to other pollutants’ vertical gradients, PAHs are expected and measured in the free troposphere (21, 22; albeit not from aircraft because of methodological limitations). The particulate phase mass fraction varies according to temperature and PM matrix, typically between 5 and 40%. All these values refer to the 16 EPA PAH
indicator substances, while other parent and oxygenated PAHs in the same samples usually are not measured.

At a few sites (9, 11, 12, 23, 24) additional parent 5–7 ring PAHs, e.g. benzo[ghi]fluoranthene, cyclopenta[cd]pyrene, triphenylene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, perylene, dibenzo[a,c]pyrene, anthracene, dibenz[a,e]pyrene, dibenz[a,h]pyrene, and coronene are monitored. Eventually, also alkyalted 2-3 ring PAHs (such as methylanthracene, 2-methylnaphthalenes, and retene (1-methyl-7-isopropylphenanthrene); Figure 1) are included in the monitoring. The concentration of alkyalted PAHs may exceed the concentration of the 16 EPA PAHs in air (25).

Nitro-, oxy- and hydroxy-PAHs have been significantly less addressed so far. Different analytical instrumentation and methods are required for trace analysis of these substances as compared to parent PAHs (26) and are not as comprehensively validated. Therefore, up until now these substances have almost nowhere been included into air monitoring programs.

Nitro-PAHs gained interest in the chemistry of nitrogen oxides rich atmospheres as tracers of photochemical pathways and sources (13). The concentration of this substance class in near-ground air was reported at \(<0.01\, \text{ng\,m}^{-3}\) at remote, low NOx sites and in the 0.01–10 ng m\(^{-3}\) range at polluted sites (21, 27–30). Nitro- and hydroxy-PAHs (31) may account for additional \(\approx 20\%\) and \(\approx 10\%\), respectively, of the 16 EPA PAH concentration in air, and oxy-PAHs for even more (29,30,32). 1-Naphthaldehyde was reported in the lower pg m\(^{-3}\) range in urban air (30).

Rarely are the 3-4 ring heterocycles dibenzofuran, dibenzothiophene and benzonaphthothiophene targeted in air (11, 23, 33, station Zeppelin, Svalbard, Norway). Interestingly, dibenzofuran was found to be the most prominent

![Figure 1: Selected polycyclic aromatic compounds found in polluted ambient air (see text). From upper left to lower right: retene, 1-nitropyrene, 3-nitro-7H-benzanthracen-7-one, dibenzofuran, dibenzothiophene, 2-amino-3,4-dimethyl-3H-imidazo(4,5-f)quinoline.](image)
species and accounted for 20–25% of the total PAH monitored on Svalbard (38 species; corresponding to 0.5–2 ng m\(^{-3}\)), sometimes exceeding the sum of EPA PAHs. In the Mediterranean and Black Seas atmosphere dibenzothiophene accounted for >50% of total PAHs (30 species; corresponding to 10–20 ng m\(^{-3}\)) (25). Chlorinated dibenzofurans and dibenzodioxins in air have attracted much interest as “classical,” legacy-related persistent organic pollutants (34). A few heterocyclic aromatic amines have been recently reported from an agricultural area in the USA (harmanes i.e., 9-H-β-carbolines, in the lower pg m\(^{-3}\) range) (35) and from ambient urban air in Beijing (up to 20 ng m\(^{-3}\) for the group of substances) (36). These N heterocycles have mutagenic and carcinogenic potential, too, and exhibit other biological effects (37). In urban air, 2-amino-3,4-dimethyl-3\(^H\)-imidazo[4,5-f]quinoline (Figure 1) accounted for 60–90% of the heterocyclic aromatic amines. It is suspected to be formed during food processing (36).

**SOURCES**

Parent and alkylated PAHs as well as some heterocycles are generally emitted from incomplete combustion of wood and fossil fuels (14). A number of nitro-PAHs are emitted from road traffic (13). Besides anthropogenic sources, natural forest fires and petrogenic (including volcanic) sources (38–40) may contribute in some environments. By means of dry and, to a lesser extent wet, deposition processes (41) PAHs are received by top soils, vegetation, and surface seawaters, and there the pollutants may accumulate due to slow biodegradation processes and transfer to downstream compartments (groundwater, deep sea). As many substances are semivolatile they are subject to revolatilisation (secondary emission) (14). The deposition flux of fluoranthene, pyrene, dimethylphenanthrenes and retene to the Mediterranean surface waters has brought these substances close and even beyond phase equilibrium, such that the direction of diffusive air-sea exchange reversed and these PAHs are nowadays at least seasonally emitted from the sea surface (25, 42).

PAH substance patterns as well as other trace substance patterns in air are used for source apportionment by characterizing substance ratios (so-called diagnostic ratios) (43) or applying multivariate statistical methods to concentration data (44). As the substance patterns of PAH sources are not being preserved during atmospheric transport, a consequence of photochemistry, and as the patterns of various relevant sources (road traffic, power plants, domestic heating, open fires) are too similar upon emission, source apportionment cannot rely on the set of PAHs commonly addressed, i.e., the 16 EPA PAHs (45). Instead, additional molecular markers for fossil fuel and wood based sources, i.e. alkanes, alkanones, alkylbenzenes, resin acids, hopanes, steranes, or sugars (32, 46–54), or other sources (alkanes, alkanones, phenols) (32, 49, 50, 52, 53) are used for attributing PAHs in air. An alkylated PAH, retene (Figure 1),
PHOTOCHEMISTRY AND LIFETIME IN AIR

Photochemical degradation of PAH in air has been investigated with a focus on the initial steps (13, 14, 57). The determination of the kinetics in the gas-phase was so far limited to the low-molecular weight parent PAHs (up to 4 rings) and the alkylated naphthalenes and phenanthrenes. Interestingly, for only 9, 4 and 7 out of the 16 EPA PAHs the reaction rate coefficients in the gas-phase with the most important oxidants in air, the hydroxyl radical, kOH, ozone, kO3, and the nitrate radical, kNO3, respectively, have been determined experimentally (14). As high-molecular weight parent PAHs (more than 4 rings) are mostly associated with the particulate phase in ambient air (in particular at low temperatures) (58, 59), photochemical degradation of these substances takes place by heterogeneous reactions. We know even less about the heterogeneous kinetics and mechanisms than we do about the homogeneous gas-phase chemistry. The reason is that the matrix influences reactivity and is very diverse: the composition, size and morphology of particles of the atmospheric aerosol vary according to major primary sources of particulate matter (PM; seasalt, mineral dust, fly ash, soot, etc.) (60) and according to photochemical age (formation of secondary inorganic and organic aerosols, cloud processing) (60, 61). Also, the physical sinks of the carrier, i.e., wet and dry deposition, may limit the lifetime of sorbed substances. A number of the 16 EPA PAHs and other parent PAHs' (acepyrene, benzo[e]pyrene, benzo[ghi]fluoranthene, benzo[ghi]perylene, coronene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, perylene) heterogeneous chemistry has been addressed in laboratory studies, but the coverage of matrix diversity and photochemical age is still very deficient. With this lack of experimental data, quantitative structure reactivity relationships or models (62) and simplifying assumptions (e.g. neglect of heterogeneous reactivity) are used to predict reactivity in exposure modeling. The ratio between the relatively fast decaying benzo[a]pyrene and the relatively stable benzo[e]pyrene (diagnostic ratio) is used as indicator for long-range transport (or aging). Atmospheric exposure modelling of polycyclic aromatic compounds is clearly lagging behind in its development when compared to the modelling of other criteria pollutants, due to lack of kinetic data but also large uncertainties in emission estimates (63). Because of the limited availability of emission estimates and monitoring data, which are needed for model evaluation, PAH modeling so far almost exclusively addressed benzo[a]pyrene (64–67) and a few semivolatile EPA PAH compounds, i.e. phenanthrene, anthracene, fluoranthene, and pyrene (68, 69).
In the gas-phase the reaction with the hydroxyl radical limits the parent PAHs’ atmospheric residence times to hours or days at most. Oxy-PAHs are formed through initial OH attack in the gas-phase or ozone reaction in the particulate phase, nitro-PAHs through initial OH or NO$_3$ attack in the gas-phase or by HNO$_3$-catalyzed NO$_2$ reaction in the particulate phase (13, 14). In this way, on sunny days nitro-PAHs are formed within hours from parent PAHs in polluted air (13). Nitro-PAHs have attracted interest because of their contribution to atmospheric oxidants formed in photo smog (health risk via inhalation, potential damage to plants including crops) (13), their suitability for source identification (isomers of e.g., nitrofluoranthe and nitropyrene are specific) (13) and as tracers for atmospheric long-range transport (21, 70). Knowledge about levels and distributions in the atmosphere and related laboratory data (14, 71) have been obtained mostly in the last decade.

The reactions on particles can be somewhat faster than in the gas-phase (on a per air volume basis) (72–75) but the effective shielding of the particle-sorbed PAH against oxidant attack by the particulate phase matrix (76) may be more relevant for atmospheric lifetimes. Indeed, PAHs carried by particles (e.g., 14, 70, 77, 78) and also nitro-PAHs (14, 21) undergo long-range transport and reach pristine areas in high altitudes and latitudes, even though kinetic data obtained in the laboratory using model PM may suggest fast degradation in air. In conclusion, reactivity in air, hence, lifetime and long-range transport potential, cannot be assessed based on quantitative knowledge for most parent PAHs, including the most toxic ones in this class of substances, and not even for the majority of the EPA PAHs. This state of knowledge is surprisingly deficient with respect to the need to characterize exposure and the long time that interest in PAHs with regard to air pollution has been on the agenda (> 3 decades) and legislative action was taken (BAP as a criteria pollutant in air in many countries).

TOXICITY OF AIRBORNE COMPOUNDS

Among the 16 EPA PAHs the potency of benzo[a]pyrene and dibenzo[a,h]anthracene are the highest (79). In recent years, evidence is mounting that among parent PAHs benzo[a]pyrene’s contribution to the health risk might be lower than the contribution of other substances among the group of EPA PAHs, e.g., dibenz[a,h]anthracene (80). The toxic equivalents calculated from the EPA PAH levels (pahTEQ) (79) typically contribute a few percent to the overall bioTEQ in PM extracts (81, 82), while up to 20% or so is attributable to nitro-PAHs (29, 83) and even more to oxy-PAHs and quinones that have been shown to possess dioxin-like potency (84, 85). 3-Nitrobenzanthrone (3-nitro-7H-benz[de]anthracen-7-one; Figure 1), emitted from diesel exhaust and found in PM in urban air (mass mixing ratio 0.6 μg g$^{-1}$) is extremely genotoxic, also in vivo (86–88). Most of the activity is associated with the
particulate phase but gaseous substances contribute, too. Some PAHs are estrogenic while other PAHs or compounds in diesel exhausts are reported to be antiestrogenic (82). The heterogeneous reaction of PAHs with ozone includes a long-lived pre-reactive complex which is a reactive oxygen species with lifetimes exceeding 100 s (89). This means a particular allergic potency.

As particle transport, deposition and inflammatory effects are very different from the gaseous noxious agents (90, 91), gas-particle partitioning and mass size distribution of PAHs are needed to be characterized in order to assess the related risk upon inhalation. PAH, oxy-, and nitro-PAH mass size distributions have been determined in recent years in polluted air, mostly unimodal. The fine fraction $<0.5 \mu m$ of aerodynamic particle size accounted for $>50\%$ or even $>90\%$ of the total PAH content (92, 93) and mass median diameters mostly in $0.5–1.4 \mu m$ sizes (94, 95). Similar findings are reported for oxy- and nitro-PAHs (30, 96). Upon emission in combustion processes (e.g., vehicle exhaust) the PAHs and derivatives seem to be associated with ultrafine particles (30).

**RESEARCH NEEDS**

No sufficiently sensitive and fast *in situ* methods exist (individual substance basis). Consequently, little is known about the temporal variability of PAH, nitro-, and oxy-PAH levels in ambient air, about the distribution in the mid and upper troposphere (airborne measurements), and the chemical processes immediately following emission in combustion processes.

Reactivity of most parent PAHs in air, hence, lifetime and long-range transport potential, needs to be better characterized quantitatively based on laboratory data of both homogeneous and heterogeneous photochemistry. These data are widely lacking today. More laboratory data are needed to describe the PM matrix, in particular the organic phases and soot, for which PAHs have a high affinity (59). Realistic PM matrices, various degrees of aerosol aging and particulate organic matter phase state need to be addressed. PAH sorption to PM needs to be better understood in order to predict gas-particle partitioning, which strongly influences atmospheric lifetimes, hence, long-range transport and exposure of remote environments.

Obviously, those species which stand for the highest toxicity should be addressed in the monitoring of ambient air. Candidates are dibenz[a,h]anthracene and 3-nitrobenzanthrone, among others. Indoor exposure is dominated by specific PAH sources such as tobacco smoking and cooking (97), not addressed in this article. Apart from characterizing exposure, an extended monitoring will expectedly improve source identification and, hence, management options. The relevance of unidentified substances could be explored by a direct combination of chemical and biological (effect directed)
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analysis of ambient samples (e.g., so-called “mutagrammes”) (98). More polycyclic aromatic compounds, not yet detected in the atmospheric environment, can be expected (non-target analysis, which is uncommon for atmospheric matrices).

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