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Analysis and occurrence of endocrine-disrupting chemicals in airborne particles

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ABSTRACT

This article presents an overview of the analytical methods for the determination of target endocrine-disrupting chemicals (EDCs) in airborne particles. Among EDCs, we selected four important groups of compounds (alkylphenols, bisphenol A, phthalates, and natural and synthetic sex hormones) because of their worldwide production, environmental ubiquity and toxicity. Due to their physical and chemical properties (high molecular weight, low/medium polarity and volatility), these EDCs can be present in the atmosphere mainly associated with particulate matter. EDCs linked to small particles (PM_{10} and $PM_{2.5}$) can penetrate into the respiratory system and damage human health. We discuss aspects of analytical methodology, such as sampling, extraction, and determination. We review levels found in outdoor and indoor samples. According to the results reported, human exposure to these compounds, especially in indoor environments, should be investigated in more depth, since some compounds, such as dibutyl phthalate and diethyl phthalate, reach levels of μg/m^3.

Contents

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1. Introduction

Endocrine-disrupting chemicals (EDCs) can affect the balance of the endocrine system in humans and animals. Some naturally occurring compounds can interfere with hormone biosynthesis, metabolism or action, resulting in deviation from normal homeostatic control or reproduction [1]. Furthermore, numerous synthetic chemicals used in industrial, agricultural and household applications have endocrine-disrupting properties.

In the past 50 years, the presence of EDCs in the environment has increased due to the growth of population and industrial and technological advances. In 1999, the European Union established the "Community Strategy for Endocrine Disruptors", which includes more than 680 substances able to damage the hormone system [2]. Research to date has mainly focused on disrupting compounds that can have negative effects in human reproduction – acting on estrogen receptors ERα and ERβ – such as the four groups considered in this work [i.e. alkylphenols (APs), bisphenol A (BPA), phthalates, and natural and synthetic sex hormones] [3].

EDCs are introduced into the aquatic environment by urban and sewage-treatment plant (STP) discharges and tend to accumulate in sediments and biota due to their hydrophobic character. Furthermore, EDCs can bioconcentrate along the food chain, damaging human health. The occurrence of EDCs in aquatic environments and biological samples has been widely reported [4–9].

Meanwhile, humans are exposed to EDCs via ingestion, inhalation and dermal pathways. Consequently, different sources of these compounds should be considered in order to ensure public safety. High levels of endocrine-disrupting pollutants were measured in food (mainly in fatty food) because of the environmental pollution and migration by contact with plastics and other materials used in processing and storage of foodstuffs [10,11]. Moreover, their presence in personal-care products, such as hair sprays, nail polishes, solvents and perfume fixatives, has also been demonstrated [12,13].

Another potential pathway of exposure to EDCs is environmental air; however, few studies about this topic can be found in the literature. The atmosphere is a geochemical reservoir of organic compounds, interacting with oceans, land and living organisms, including human beings [14]. Partitioning between gas phase and airborne particles is also common. The fraction associated with airborne particles increases with higher values of molecular weights (MWs) and lower values of vapor pressure [15]. As a result, EDCs can be inhaled, penetrate into the respiratory system and be deposited in the lungs, where they are adsorbed to inhalable atmospheric particles PM_{10} (coarse particles, less than 10 μm in diameter) or $PM_{2.5}$ (fine particles, less than 2.5 μm in diameter). Significant correlation of particulate matter (PM) with mortality has been demonstrated in different studies of respiratory diseases [16]. Recently, the International Agency for Research on Cancer (IARC) and the World Health Organization (WHO) announced that there is convincing evidence that exposure to outdoor air pollution causes lung cancer, and it has been classified as carcinogenic to humans (Group 1). PM, a major component of outdoor air pollution, was evaluated separately and also classified as carcinogenic to humans (Group 1) [17].

The damage to human health increases in closed places due to poor ventilation and slow chemical-degradation processes [18]. People spend about 90% of time in cars, houses and offices, so indoor air requires greater attention [19]. The measured concentrations of EDCs in indoor air are higher than those in outdoor air because of the use of plasticizers and other compounds, such as polybrominated diphenyl ethers (used as flame retardants) in the production of buildings and furniture [19,20]. As a result, indoor air is one of the most serious environmental risks to public health that also needs to be taken into account [21].

Although exposure to EDCs via air can occur outdoors and indoors, specific knowledge concerning potential human health effects of these EDCs is still limited. These EDC pollutants could act additively or have antagonistic or other interactive effects by operating at different points in cell-signaling systems [21]. Because exposure to mixtures is critical in health effects, simultaneous multiclass investigations of different EDCs are required.

2. Specific groups of endocrine-disrupting chemicals

This review focuses on four classes of semi-volatile EDCs with similar disrupting properties. Table 1 shows their physical and chemical properties and estrogenic activity.

Vapor-pressure values (between 10^{-13} mmHg and 1 mmHg) indicate that these compounds can volatilize and be present in the atmosphere [25]. In addition, their octanol-water partition coefficients (K_{ow}) show their tendency to be associated with PM.

2.1. Natural and synthetic sex hormones

Natural and synthetic sex hormones have been widely used in daily life and in the livestock industry for various purposes, such as contraception, human and veterinary therapy, and growth promotion [15]. They include biogenic hormones, such as 17β-estradiol (E2) and their metabolites estrone (E1) and estriol (E3), and synthetic chemicals such as 17α-ethynylestradiol (EE2), used mainly as a contraceptive, and diethylstilbestrol (DES).

Table 1
Physicochemical properties and estradiol equivalent factors of target endocrine-disrupting chemicals

Compound	Molecular weight	Log K_{ow}	Vapor pressure (mm Hg)	Henry's law constant (atm m^3/mole)	EEF
Estrone	270.37	3.13[a]	1.42E-007[a]	3.8E-010[a]	0.01–0.20[c]
17-β-Estradiol	272.39	4.01[a]	1.26E-008[a]	3.7E-011[a]	1[c]
Estriol	288.39	2.45[a]	1.97E-010[a]	1.3E-012[a]	0.46[c]
17-α-Ethynyl estradiol	296.41	3.67[a]	2.67E-009[a]	7.9E-012[a]	1.25[c]
Diethylstilbestrol	268.36	5.07[a]	1.41E-008[a]	5.8E-012[a]	1.25–8[c]
4-tert-octylphenol	206.33	4.12[b]	3.6E-004[b]	4.5E-006[b]	1E-005-8E-004[c]
Nonylphenol	220.34	4.48[b]	9.5E-005[b]	5.9E-006[b]	2.3E-005-9E-004[c]
Bisphenol A	228.29	3.40[b]	8.7E-010[b]	9.8E-011[b]	2.3E-005-6E-004[c]
Dimethyl phthalate	194.20	1.61[b]	1.7E-003[b]	9.5E-008[b]	1E-006[d]
Diethyl phthalate	222.20	2.54[b]	4.8E-005[b]	2.4E-007[b]	5E-007[d]
Dibutyl phthalate	278.35	4.27[b]	7.3E-005[b]	1.3E-006[b]	1E-007[d]
Diethylhexyl phthalate	390.56	7.73[b]	9.8E-008[b]	3.9E-005[b]	1E-006[d]

EEF, Estradiol equivalent factor; Log K_{ow}, Octanol-water partition coefficient.
[a] [22].
[b] [23].
[c] [7].
[d] [24].