atmosphere

MDPI

Article

Atmospheric Estrogenic Semi-Volatile Compounds and PAH in $PM_{2.5}$ in Mexico City

José Gustavo Ronderos-Lara [1], Fernando Millán-Vázquez [1], Mario Alfonso Murillo-Tovar [2], Hugo Albeiro Saldarriaga-Noreña [2], Brenda Liz Valle-Hernández [1], Khirbet López-Velázquez [3] and Violeta Mugica-Álvarez [1],*

[1] División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Azcapotzalco Azcapotzalco, Ciudad de Mexico 02128, Mexico; ronderos92@gmail.com (J.G.R.-L.); fernandomillan117@gmail.com (F.M.-V.); blvh@azc.uam.mx (B.L.V.-H.)

[2] Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Cuernavaca 62209, Morelos, Mexico; mario.murillo@uaem.mx (M.A.M.-T.); hsaldarriaga@uaem.mx (H.A.S.-N.)

[3] CONAHCyT, Universidad Politécnica de Tapachula, Tapachula 30830, Chiapas, Mexico; khirbet74@gmail.com

* Correspondence: vma@azc.uam.mx

Abstract: The quantification of semi-volatile organic compounds with potential endocrine-disrupting activity contained in fine atmospheric particles ($PM_{2.5}$) is essential to understand their temporal behavior, identify their sources, and evaluate the health risks resulting from population exposure to said compounds. Since information and research outcomes regarding their presence in the atmosphere in developing countries are scarce, the main objective of this work was the development of a methodology devoted to extracting, characterizing, and quantifying, for the first time in Mexico, the concentration levels of three important groups of endocrine-disrupting compounds (EDCs) bonded to $PM_{2.5}$ and collected during a year, namely: alkylphenols (4-n-nonylphenol (4NP) and 4-tert-octylphenol (4tOP)); bisphenols (bisphenol A (BPA) and bisphenol F (BPF)); natural and synthetic hormones (17β-estradiol (E_2), estriol (E_3) and 17α-ethinyl estradiol (EE_2)). Further, priority polycyclic aromatic hydrocarbons (PAH) that also disrupt endocrine activity were analyzed. All compounds were determined by gas chromatography coupled to tandem mass spectrometry, and the concentration levels were analyzed for different climatic seasons. Cold-dry (CD) season displayed higher levels of 4NP, bisphenols, and hormones (between 0.71 (4NP) and 1860 pg m^{-3} (BPA)), as well as PAH concentrations (9.12 ng m^{-3}). Regarding health effects, concentrations of alkylphenols, bisphenols, and hormones quantified had a value of estradiol equivalent concentration (EEQ_{E2}) between 0.07 and 0.17 ng m^{-3}. PAH concentrations did not have carcinogenic and mutagenic risk with $BaP_{(PEQ)} < 1$ ng m^{-3}. These results can be used by policymakers in the design of strategies for air pollution control.

Keywords: $PM_{2.5}$; endocrine disruptors; bisphenols; alkylphenols; hormones; PAH; Mexico City

check for updates

Academic Editor: Daniele Contini

Received: 30 December 2024
Revised: 26 January 2025
Accepted: 30 January 2025
Published: 5 February 2025

Citation: Ronderos-Lara, J.G.; Millán-Vázquez, F.; Murillo-Tovar, M.A.; Saldarriaga-Noreña, H.A.; Valle-Hernández, B.L.; López-Velázquez, K.; Mugica-Álvarez, V. Atmospheric Estrogenic Semi-Volatile Compounds and PAH in $PM_{2.5}$ in Mexico City. *Atmosphere* **2025**, *16*, 178. https://doi.org/10.3390/atmos16020178

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

In agreement with the World Health Organization (WHO), atmospheric particles cause millions of premature deaths annually. Their health impact depends on both their composition, comprising organic and inorganic species, and their size; currently, $PM_{2.5}$ particles have shifted attention from total suspended particles (TSP), with thermodynamic diameters up to 60 µm and even from particles with diameters smaller than 10 µm PM_{10}, because they can penetrate deeply into the lungs and even enter in the bloodstream; $PM_{2.5}$ contribute between 40 and 58% of $PM_{10,}$ and between 15 and 25% of TSP [1–3]. Short exposure to $PM_{2.5}$ has been linked to adverse health effects, including increased hospitalizations for pulmonary obstruction, asthma, and pneumonia, while chronic exposure has been related to the development of chronic bronchitis, asthma, and emphysema [4].

Currently, fine particles have been characterized through different studies, evidencing that many compounds are trapped or adsorbed on $PM_{2.5}$ surfaces, such as heavy metals [5], soluble inorganic ions [6], polycyclic aromatic hydrocarbons [7], and organic aerosols [8], among others. Recently, it has been documented that the fine suspended particles have endocrine-disrupting potential since they could induce several estrogenic, antiestrogenic, androgenic, and antiandrogenic effects [9]. Nevertheless, information about the presence of semi-volatile organic compounds (SVOC) presenting endocrine disruption in $PM_{2.5}$ is still scarce. This lack of information brings about a relevant opportunity to enlarge knowledge about the presence of endocrine-disrupting compounds (EDCs) in the atmosphere that impact the population's health since these species are exogenous compounds that alter hormone regulation in humans and animals, affecting their reproduction and developmental function [10]. Among the reported EDCs included in particles are alkylphenols (4n-nonylphenol (4NP) and 4-*tert*-octylphenol (4tOP)), bisphenols (bisphenol A (BPA) and bisphenol F (BPF)), as well as natural and synthetic hormones (17β-estradiol (E_2), estriol (E_3) and 17α-ethinylestradiol (EE_2)), phthalates (diethylphftalate, dibutylphtalate), parabens (methylparaben, butylparaben), and polyfluoroalkyl substances. These can be released into the atmosphere as a consequence of their intense use in productive processes, industrial emissions, uncontrolled garbage burning, and electronic or unregulated handling of pharmaceutic wastes [9,11,12]. Moreover, the polycyclic aromatic hydrocarbons (PAH), which have been widely studied due to their carcinogenic and mutagenic activity, can also alter reproductivity, embryotoxicity, and endocrine disruptions affecting human homeostasis [13,14].

Aside from the aforementioned, in general, the main endocrine disruptive effects of EDCs include malformations during development, interference with reproduction, increased risk of cancer, and disturbances in immune and nervous system functions. Disruptions in the human body can occur in different ways, either through mimicking natural hormones, blocking the effects of a hormone on certain receptors, or direct stimulation or inhibition of the endocrine system, overproducing or underproducing natural hormones [3,10]. EDC estrogenic activity has been measured as an equivalent estrogenicity factor in comparison with activity from natural estrogen E_2 [15]. In humans, the interaction with alkylphenols is associated with breast cancer [16] since 4-nonylphenol can stimulate the proliferation of MCF7 breast cancer cells [17,18]. Interaction with bisphenols is related to the development of obesity symptoms, diabetes (type 2), cardiovascular disorders, polycystic ovary syndrome, reduced sexual libido, as well as decreased sperm count and quality [19,20]. BPA can cause negative alterations in personality, as well as adverse sexual effects in men [21]. Diabetes type 2 can be developed due to BPA, which can reduce insulin secretion on β-cell [22]. Low male fertility levels can be caused by BPA exposure since it can alter mitochondrial functions, decreasing ATP levels in spermatozoa, which inhibits sperm mobility quality [23]. The interaction with synthetic and natural hormones is linked to the development of breast cancer [24], prostate cancer [25], and cardiovascular diseases [26]. Biological high levels of E_2 [27] and exogenous E_2 and EE_2 (as oral contraceptives) are related to the development of breast cancer in women due to mutations in high penetrance tumor suppressor genes: BRCA1 (BReast-CAncer 1) and BRCA2 [28–30]. Regarding PAHs, several assays have shown that they can disrupt endocrine systems, modulate estrogen pathways, and induce oxidative stress in certain organisms [14,31].

EDCs present different molecular properties; therefore, their action mechanism is different in the endocrine system, and this could be used to evaluate a broad spectrum of disruption disorders in the population. Additionally, due to their wide application and high demand in industrial production, they can persist in the atmosphere, adsorbed in particles, and become capable of entering the human body through the respiratory process. Some studies have shown the presence of SVOC, such as alkylphenols, bisphenols, and hormones in PM_{10} and $PM_{2.5}$ in different countries. BPA was identified in PM_{10} in the United States of America [32], India [11]) and Greece [33], whereas $PM_{2.5}$ was measured in China [11] and Spain [12]; in this last study, E_2, E_3, EE_2, and 4NP were also detected. Additionally, 4NP and 4tOP were determined in Greece [33], Japan [34] and France [35]. Other studies have detected alkylphenols, bisphenols, and hormones in particles, but in those, the particle sizes were not reported; BPA, 4NP, and 4tOP were identified in Germany [36]. Exceptionally, the sampling period of EDC studies has been short (from days to months) [32,33], which does not allow seasonal analysis. In contrast to the EDCs mentioned above, many studies have reported the presence of PAH in atmospheric particles in several countries, such as Argentina [37], China [38], Central India [39], Spain [40], and Mexico City [41,42]. Gas chromatography (GC) coupled to mass spectrometry (MS) or tandem MS (MS/MS) has been mostly a common technique used for the identification and quantification of semi-volatile EDCs, where electron ionization is usually employed, although to better resolution, a previous derivatization step is usually required; although few works have been reported the use of liquid chromatography coupled to mass spectrometry (LC-MS), this technique does not need derivatization and has superior performance in terms of ionization efficiency and sensitivity for EDCs analysis in particles [12].

As far as our knowledge allows, studies in Mexico focused on determining alkylphenols, bisphenols, and hormones contained in PM, as well as the potential health risks caused by this kind of EDC in the atmosphere, have not been conducted. Notwithstanding that PAH has been studied in the atmosphere of Mexico City, more research is still needed to follow their trends due to their estrogenic activity and carcinogenic properties in addition to the determination of other families of compounds that could be associated with health impacts related to endocrine disruption.

The key distinction between developed countries, where EDCs have been studied, and Latin America lies in the scarcity of information to understand the behavior, distribution, and fate of these compounds in the atmosphere. This knowledge gap is a challenge for authorities' health when assessing diseases associated with endocrine disruption that are correlated with the presence of these compounds.

In order to generate information related to the levels of EDC in $PM_{2.5}$, in this study, an analytical method was developed to determine the temporal variation in the most widely studied species of estrogenic compounds 4NP, 4tOP, BPA, BPF, E_2, E_3, and EE_2, which can be detected by chromatography after the same step of derivatization; in addition, the priority PAHs were quantified in an industrial and populated area located upwind, which impacts a large part of the city. Furthermore, the seasonal behavior of concentrations and the estrogenic activity due to the alkylphenols, bisphenols, and hormones were compared, and the potential risk of cancer and mutagenicity due to PAH was determined. The information generated will be useful for environmental and health policymakers to relate air pollution with estrogenic diseases and for other researchers worldwide to assume a deeper concern for this health menace.

2. Materials and Methods

2.1. Sampling Site

Mexico City is the capital of Mexico, with a territory of 1494 km^2. In 2020, the population was 9.2 million inhabitants [43]. Additionally, in 2022, 6,368,520 vehicles, including trucks and cargo vans, were reported in Mexico City [44]. Moreover, in 2023, there were about 4500 established industries dedicated to food processing or activities that require the use of chemical, biological, or pharmaceutical compounds [45]. The sampling was carried out at the Autonomous Metropolitan University—Azcapotzalco (9°30′13.6″ N 99°11′09.0″ W), located north of Mexico City and close to an industrial area in which the main activities are the machinery and equipment production, food, beverages, chemicals, and petroleum products [46], the traffic is high and there are a large number of unregulated street food stalls using wood or carbon. Additionally, this site is considered an emission site of particles since it is upwind of the city and has a meteorological station. Several studies have been conducted there, and this research will contribute to complement particle characterization [6,41].

2.2. Sampling

Sampling was performed based on the recommendations established by the EPA regarding the procedure for sampling ambient air [47]. The $PM_{2.5}$ samples were collected in a Hi-Vol equipment (Tisch) with an average flow of 1.13 m^3 min^{-1} using a quartz filter (20 × 25 cm) previously calcined in a muffle at 800 °C for 3 h. Sampling was conducted every 6 days from July 2021 to June 2022 for 24 h; in order to understand the temporal variations due to temperature and meteorological changes across the year, three seasons were considered: rainy season (R) from July to October, cold-dry season (CD) from November to February and hot-dry season (HD) from March to June. After sampling, filters were transported to the laboratory and stored at −4 °C until analysis.

2.3. Chemicals and Reagents

All solvents and gases employed were of chromatographic grade. Acetone and hexane were obtained from Honeywell (1953 S. Harvey St., Muskegon, MI, USA). The standards: 4-nonylphenol (4NP; linear isomer), 4-tert-octylphenol (4tOP), 17β-estradiol (E_2), estriol (E_3), 17α-ethinylestradiol (EE_2), bisphenol A (BPA), bisphenol F (BPF) and surrogates: deuterated 17β-estradiol (E_2-d_2) and deuterated bisphenol A (BPA-d_{16}), as well as derivatizing N,O-Bis(trimethylsilyl) trifluoroacetamide with trimethylchlorosilane (BSTFA + TMCS (99:1)) and pyridine were supplied by Sigma-Aldrich (St. Louis, MO, USA). Deuterated chrysene (Chr-d_{12}) was purchased from Supelco (Bellefonte, PA, USA). Priority PAH standards, Naphthalene (Nap), 2-Methylnaphthalene (2-Mnap), Acenaphthylene (ACL), Acenaphthene (AC), Fluorene (Fl), Phenanthrene (Phe), Anthracene (AN), Fluoranthene (FA), Pyrene (Py), Retene (Ret), Benzo[a]Anthracene (BaA), Chrysene (Chr), Benzo[k]Fluoranthene (BkFA), Benzo[b]Fluoranthene (BbFA), Benzo[a]Pyrene (BaP), Indene[c,d]Pyrene (IcdP), DiBenzo[a,h]Anthracene (DBahA), and Benzo[g,h,i]Perylene (BghiP) were purchased from Sigma Aldrich (St. Louis, MO, USA).

2.4. Extraction and Derivatization

The extraction of alkylphenols, bisphenols, and hormones carried out by ultrasound-assisted extraction (UAE) in a water bath (ambient temperature) was optimized using different solvents based on the proposed method by Ronderos et al., applied to sediments [48]. Briefly, 85.5 cm^2 filter area was spiked with 30 ng (dissolved in 100 µL of acetone) of BPA-d_{16} and E_2-d_2 as surrogates. After spiking, the filter samples were cut into small pieces and stored under refrigeration (4 °C) overnight. For extraction, three solvent mixes (*v*:*v*) were prepared: hexane-dimethyl chloride (DMC) (1:1), acetone-DMC (1:1), and hexane-acetone (1:1 *v*:*v*). Then, 40 mL of each mixture was added to three samples and sonicated for 20 min, and this procedure was repeated using a clean solvent mixture. After the extraction, the liquid phases were combined, and resulted volume was evaporated by rotary-evaporation to about 1 mL, which was filtered through a nylon acrodisc (0.20 μm × 13 mm) and collected. Then, the filtrated sample was dried under a gentle stream of nitrogen until complete dryness for further derivatization, which was performed by the addition of 50 μL of BSTFA + TMCS (99:1) and 50 μL of pyridine in a thermostatic bath at 70 °C. After derivatization, vials were kept at room temperature, and the internal standard was added (Chry-d_{12}, 1500 ng mL^{-1} dissolved in the derivatizing:pyridine (1:1 *v*:*v*) mix). This procedure was applied to all samples, using the best solvent mix that turned out to be hexane-acetone (1:1 *v*:*v*).

For PAH extraction, the methodology proposed by Valle Hernandez et al. [49] was applied. Briefly, 85.5 cm^2 of each sample filter was immersed in 30 mL of methylene chloride. Prior to extraction, 250 ng of deuterated PAH was added to the sample filters. Then, the samples were sonicated twice for 30 min in a water bath using a cooling device to avoid evaporation and analytes losing. The extracts were combined and concentrated until 1 mL in a rotary evaporator at 30 °C (bath water) and 5 inHg vacuum pressure for further filtration through syringe filters and brought to 1 mL.

2.5. Method Validation and Extraction Optimization

Linearity was determined by the correlation coefficient (r) obtained from a calibration curve with seven different concentration levels (0–300 ng mL^{-1}). The limit of detection (LOD) and limit of quantification (LOQ) were determined from the calibration plot, using the concentration providing a signal equal to the blank signal (Y_B = Sy/x), plus three times and ten times, respectively, the standard deviation of the blank (S_B = a).

The optimization of the extraction method consisted of determining the best chromatography area obtained with acetone-hexane (1:1 *v*:*v*), acetone-dichloromethane (1:1 *v*:*v*), and hexane-dichloromethane (1:1 *v*:*v*). The extraction method was validated by assessing recovery efficiency (%) without surrogates (external standard) and recovery with surrogates, and precision was evaluated by repeatability, expressed as relative standard deviation (RSD) of the response.

Quantification of compounds was performed using the surrogate standard method with deuterated compounds. The E_2-d_2 surrogate was assigned to E_2, E_3, and EE_2, while the BPA-d_{16} surrogate was assigned to BPA, BPF, 4NP, and 4tOP. For PAH quantification, deuterated IS all-in-one (PAH CHIRON) was used as a surrogate: Naphthalene-d_8 (Nap-d_8), Acenaphthylene-d_8 (ACL-d_8), Acenaphthene-d_{10} (AC-d_{10}), Fluorene-d_{10} (FL-d_{10}), Phenanthrene-d_{10} (Phe-d_{10}), Anthracene-d_{10} (AN-$_{10}$), Fluoranthene-d_{10} (FA-d_{10}), Pyrene-d_{10} (Py-d_{10}), Benzo[a]anthracene-d_{12} (BaA-d_{12}), Chrysene-d_{12} (Chr-d_{12}), Benzo[k]fluoranthene-d_{12} (BkFA-d_{12}), Benzo[a]pyrene-d_{12} (BaP-d_{12}), Benzo[b]Fluoranthene-d_{12} (BbFA-d_{12}), Indeno [1,2,3-cd]Pyrene-d_{12} (IcdP-d_{12}), Benzo[ghi]Perylene-d_{12} (BghiP-d_{12}) and Dibenzo[a,h]Anthracene-d_{14} (DBahA-d_{14}).

2.6. Risk Assessment for Estrogenic Compounds

Due to the potential of the studied compounds to promote adverse health effects, the concentration of these compounds in $PM_{2.5}$ was assessed in terms of estrogenic activity as estradiol (E_2) equivalent concentration (EEQ_{E2}) [15]. This was estimated as the product of each compound concentration and its corresponding estradiol equivalent factor (EEF).

Estrogenic activity was assessed for 4NP, 4tOP, BPA, E_2, E_3, and EE_2, applying the EEF values determined by Céspedes et al. [50]. EEQ was determined with Equation (1):

$$\mathrm{EEQ_{E2}} = \mathrm{C_i} \times \mathrm{EEF_i} \tag{1}$$

where C_i is the concentration determined in the sample for compound i, and EEF_i is the estradiol equivalent factor for compound i.

For each sample day, ΣEEQ_{E2} due to inhalation exposure was determined for children and adults using Equation (2).

$$\Sigma\mathrm{EEQ_{E2}} = \Sigma\mathrm{C_i} \times \mathrm{EEF_i} \tag{2}$$

The concentration intake of 4NP, 4tOP, BPA, E_2, E_3, and EE_2 due to the respiratory process was determined for children (1–2 years old), adolescent (15–18 years old), and adult (19–65+ years old) females and males according to the US-EPA [51].

2.7. Carcinogenic and Mutagenic Potential Due to PAH

Some PAH and their metabolites have demonstrated endocrine-disrupting capabilities with varying degrees of estrogenic effects. Nevertheless, specific EEF values are not well documented [31]. Carcinogenic and mutagenic potency due to the PAH exposition were estimated as BaP equivalent ($BaP_{(PEQ)}$), with related potential equivalent factor (PEF) and mutagenic equivalent factor (MEF). The risk of cancer was determined for compounds using PEF and MEF values [52,53] through Equations (3) and (4):

$$\mathrm{Bap_{(PEQ)}} = \Sigma\mathrm{C_i} \times \mathrm{PEF_i} \tag{3}$$

$$\mathrm{Bap_{(MEQ)}} = \Sigma\mathrm{C_i} \times \mathrm{MEF_i} \tag{4}$$

where C_i is the concentration of each PAH; PEF_i corresponds to the carcinogenic potential equivalency factor, and MEF_i corresponds to the mutagenic equivalency factor relative to BaP.

2.8. Chromatographic Analyses

Analyses of estrogenic compounds were performed in an AGILENT 6890 chromatograph coupled to a triple quadrupole mass spectrometer (7000D), using an HP5-MS column (30 m × 250 μm × 0.25 μm), helium (99.9999%) as a carrier gas (1 mL min^{-1}), while nitrogen (1.5 mL min^{-1}) was used in the reaction cell (second quadrupole). Conditions such as temperature, as well as voltages (eV) applied in the mass spectrometer and transitions selected for the identification of compounds, are shown in the Supplementary Material (Table S1).

PAH separation and their identification were conducted by GC-MS in an Agilent Technologies chromatograph (5973) coupled to a mass spectrometer with an HP5-MS column (30 m × 250 μm × 0.25 μm) with helium (99.9999%) as a carrier gas (1.2 mL min^{-1}).

The column's temperature started at 40 °C and was maintained for 1 min. Then, it was increased by 15 °C every minute until reaching 250 °C, with increments of 5 °C per minute until reaching 300 °C. The transfer line from the chromatograph to the mass spectrometer was kept at 310 °C. The ionization of molecules was carried out by electronic impact (EI), and the ionization source temperature was kept at 200 °C.

2.9. Quality Assurance/Quality Control (QA/QC)

After heating the material, the temperature was set to room temperature, and it was wrapped with aluminum foil (heated at the same time as the material). All materials were stored in a BPA-free plastic box until use. To avoid concentration overestimation due to the alkylphenols and BPA ubiquity, solvent blanks were analyzed during instrumental analysis. Sample analysis was divided into sample batches, each containing three samples and to avoid concentration overestimation due to the presence of alkylphenols and BPA, solvent blanks were analyzed in every new batch of analysis.

Chr-d_{12} (1000 ng mL^{-1}) standard was analyzed after blank analysis to determine variations due to equipment operation and reference solutions. When the variation response was bigger than 5%, an electronic blank, a blank solvent, and a reference solution were injected before continuing with analyses.

3. Results

3.1. Method Validation and Optimization

The correlation coefficient (r) varied in the 0.9947–0.9999 range for all compounds. A linear working range was set for 4tOP at 0–150 ng mL^{-1}, while for the rest of the compounds, it was set from 0 to 300 ng mL^{-1}.

LOD varied between 0.04 ng mL^{-1} for E_2 and E_3 and 8.2 ng mL^{-1} for BPA, while LOQ varied between 0.13 ng mL^{-1} (E_2) and 27.35 ng mL^{-1} (BPA). Complete information about method validation (Table S2) and the chromatogram obtained for the analysis can be found in the Supplementary Material (Figure S1).

For the selection of the best extraction solvent mix, the hexane-DMC (1:1, *v*:*v*) showed major chromatography areas for 4NP, 4tOP, E_2, and EE_2 (Figure 1). However, chromatography areas for BPA were small, indicating that during analyses of samples with small concentrations, the BPA signal could be absent (Figure 1). Conversely, extractions with hexane-acetone (1:1 *v*:*v*) attained greater chromatography areas than those for extractions with acetone-DMC (1:1 *v*:*v*) for all compounds, with the exception of E_3, which was slightly lower. Thus, hexane-acetone (1:1 *v*:*v*) was selected as the best solvent mix for extraction.

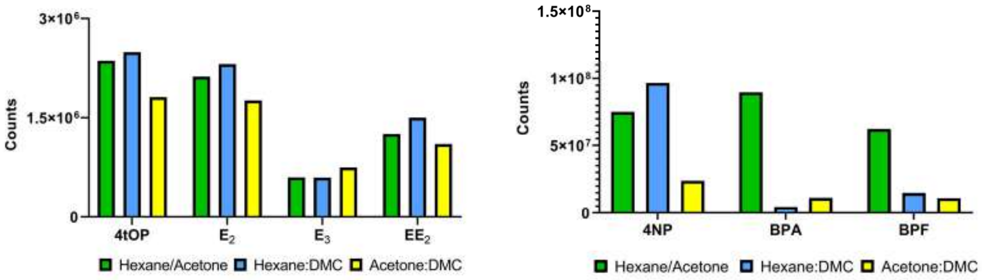


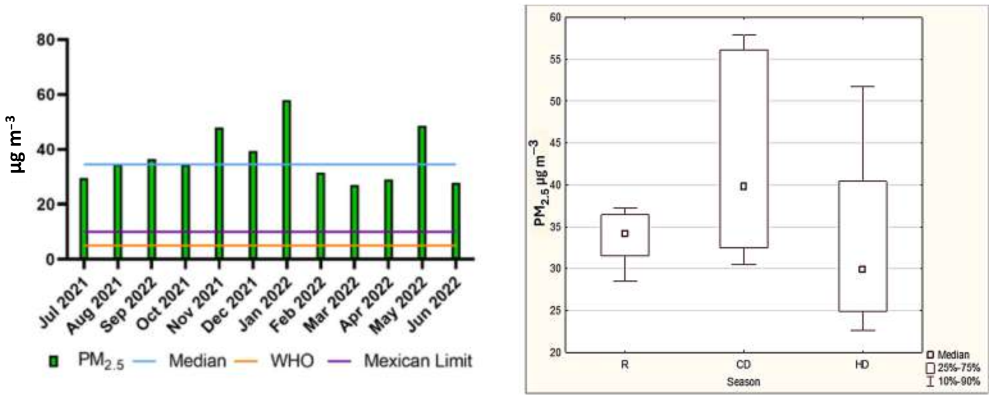
Figure 1. Chromatography area for estrogenic EDCs obtained for extraction with different solvents. DMC = dichloromethane; graphics were separated to avoid suppression bars.

A hexane-acetone solvent mix was employed to extract 4NP, 4tOP, and BPA [36]. Nonetheless, according to the literature, this solvent mix has not been used before for BPF, E_2, E_3, and EE_2 extraction, which presents an alternative to the development of methodologies that require simultaneous extraction of this kind of compounds.

For validation of the extraction method, recoveries were determined using external standard and surrogated methods. External standard recoveries varied between 50.85% (E_3) and 114.66% (BPA), while surrogated standard recoveries varied between 73.86% (4NP) and 110.12% (BPF). Recoveries for all compounds are summarized in Supplementary Material (Table S2). Surrogate standard recoveries obtained comply with US-EPA extraction guidelines that establish recoveries between 70% and 130% for environment samples [54]. Therefore, the extraction method is efficient and reliable when applied to the EDCs contained in particles.

3.2. $PM_{2.5}$ Concentration in the Mexico City Atmosphere

From July 2021 to June 2022, the total $PM_{2.5}$ mass varied between 22.65 μg m^3 (HD season) and 57.88 μg m^{-3} (CD season), with an annual median concentration equal to 35.02 μg m^{-3} (Figure 2). It is worth mentioning that this value is seven times higher than the proposed by WHO guidelines (5 μg m^{-3}) for air quality [55]. Also, annual median concentrations determined were almost three times higher than the proposed levels by Mexican authorities, as 10 μg m^{-3} [6]. These concentrations can be attributed to the high activity in the industrial area, not only due to industrial processes but also because of the heavy traffic of freight transport vehicles. Applying the Mann–Whitney test ($p \leq 0.05$), no significant differences in median $PM_{2.5}$ concentrations were found between HD and R; meanwhile, significant differences ($p > 0.05$) were observed between CD and R and between CD and HD seasons, suggesting that unfavorable conditions for pollutant dispersion prevail in the CD season due to an increase in the consumption of fossil fuels, frequent during this period, that has been associated with higher particle concentrations, as well as stable meteorological conditions. The high concentration reported in May is attributed to several forest fires that occurred in that month. Monthly and median $PM_{2.5}$ concentrations during seasons are shown in Figure 2.



(**a**) (**b**)

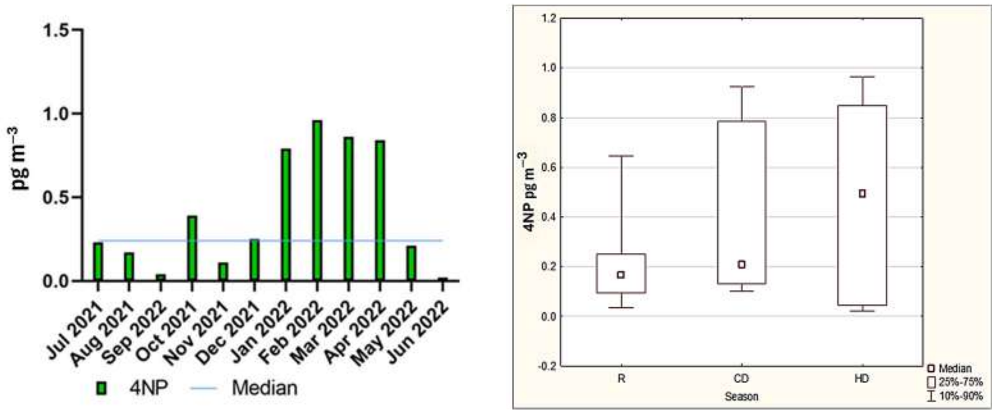
Figure 2. (**a**) Concentration of $PM_{2.5}$ determined for samples throughout the sampled year; (**b**) Median concentration of $PM_{2.5}$ determined for each season.

3.3. Estrogenic Semi-Volatile EDCs Concentrations Contained in $PM_{2.5}$

Estrogenic semi-volatile EDCs and PAH of interest were detected in all samples. Throughout the year, the average concentration for compounds decreases in the order ΣPAH > BPA > BPF > 4tOP > E_3 > E_2 > EE_2 > 4NP.

Alkylphenol and 4NP were detected in concentrations up to 1.52 pg m^{-3}, with an annual median concentration of 0.2 pg m^{-3} and median seasonal concentrations of 0.17 to 0.49 pg m^{-3} (Figure 3). These low 4NP concentrations could result from two principal factors: the rapid photochemical degradation with a half-life of 10–15 h [56] and the affinity of 4NP to the gas phase in the atmosphere instead of the particulate phase [36,57] due to its vapor pressure and its Henry's law constant.

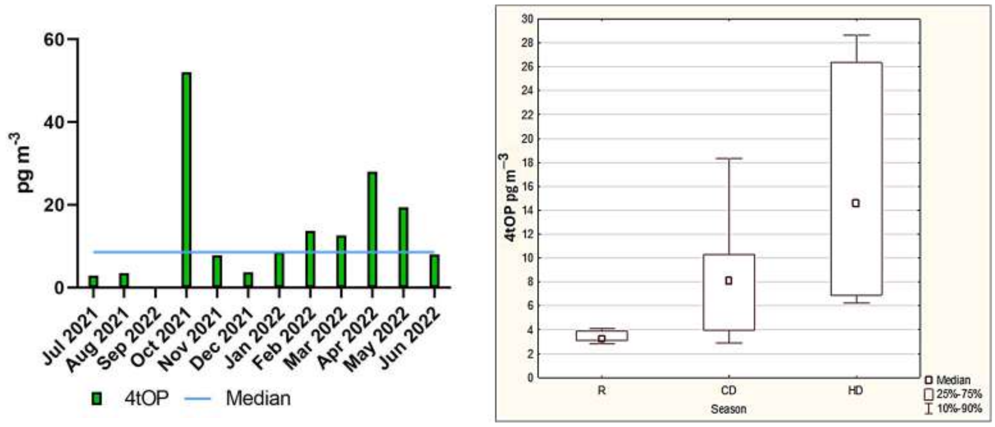
Man–Whitney test ($p \leq 0.05$) showed significant differences for R and HD seasons, probably due to the hydrophilic properties of 4NP. This behavior is consistent with observations in Germany and Belgium where 4NP was determined in rainwater [58]; 4NP concentration increases in the HD in places close to agricultural areas during grain cultivation by the use of pesticides, which contain polyethoxylates (that can result in 4NP metabolites) to improve their dispersion upon crops [15,59].



(**a**) (**b**)

Figure 3. (**a**) 4NP concentration determined throughout the sampled year; (**b**) Median concentration of 4NP determined for each season.

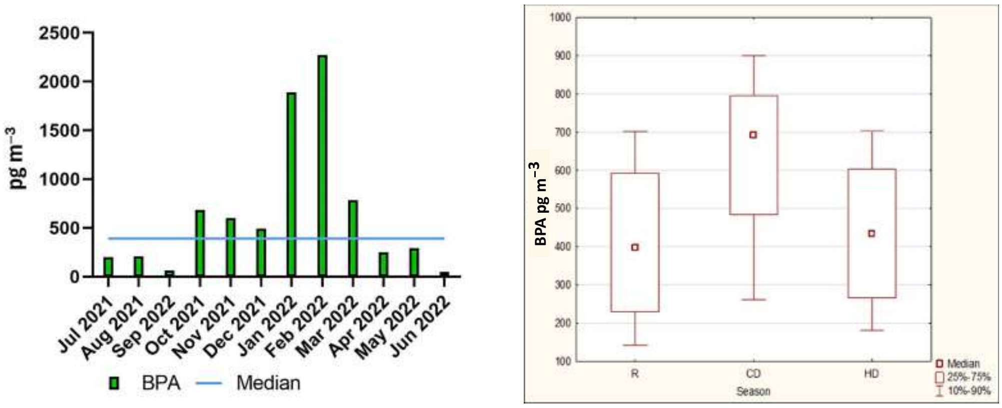
Regarding 4tOP, it was detected in concentrations between 2.36 and 89.47 pg m^{-3}, with a median annual concentration of 8.1 pg m^{-3} (Figure 4); seasonal median concentrations varied from 3.99 to 14.5 pg m^{-3}. 4tOP median concentrations were up to twenty times higher than those detected for 4NP because this last compound has high vapor pressure and a speed rate of photochemical degradation, as was mentioned before, although both compounds showed the same pattern concentrations during seasons; 4tOP is used to produce phenolic resins, used as an adherent in the vulcanization process of rubber tires manufacturing [60]. Additionally, the reaction between ethylene oxide and 4tOP produces the corresponding alkylphenol ethoxylate, which is widely used as a surfactant in the soap and degreaser processes. Likewise, a wide variety of ethoxylates are constantly synthesized or employed for the production of paper, herbicides, pesticides, emulsifiers, humectants, dispersing agents, anti-static agents, emulsifiers, and solubilizers [61]. Significant differences for 4tOP were found between CD and HD seasons and HD and R seasons ($p \leq 0.05$). Just like 4NP, relatively high concentrations of 4tOP could be due to the degradation of polyethoxylates employed in pesticide formulations since their degradation can result in 4tOP [62]. Additionally, wastewater treatment plant discharges are important emission sources of 4NP and 4tOP to the aquatic environment [63] due to the nonylphenols Henry's law constants (3 to 4 $\times$ 10^{-5} atm m^3 mol^{-1}), which enable their transference from water bodies to atmosphere [57,63].



(**a**) (**b**)

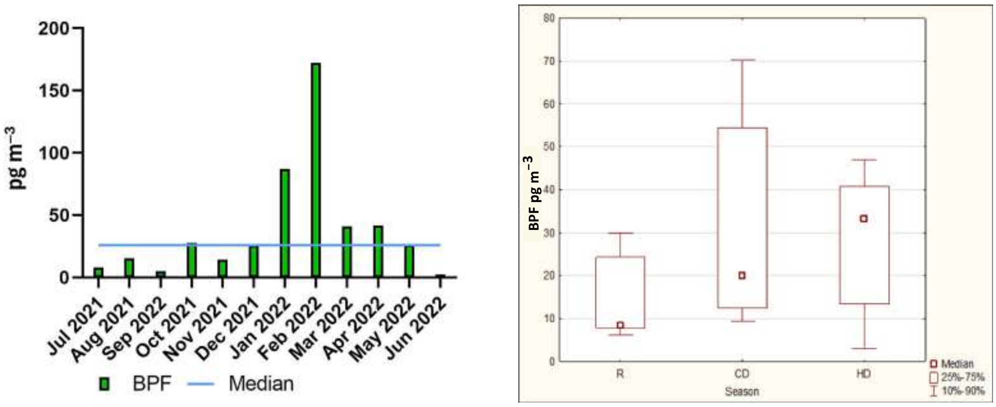
Figure 4. (**a**) 4tOP concentration determined throughout the sampled year; (**b**) Median concentration of 4tOP determined for each season.

Bisphenols BPA and BPF displayed the largest concentrations in relation to alkylphenols and hormones. BPA concentrations ranged from 24.3 to 2694 pg m^{-3} (Figure 5); this high variation in BPA has been documented in other countries such as China and Greece [11,33]. Likewise, BPA median concentrations decreased in the order CD > HD > R, while BPF concentrations were between 0.88 and 283.14 pg m^{-3} (Figure 6). BPF median concentrations in the seasons decreased in the same order as BPA.



(**a**) (**b**)

Figure 5. (**a**) BPA concentration determined throughout the sampled year; (**b**) median concentration of BPA determined for each season.



(**a**) (**b**)

Figure 6. (**a**) BPF concentration determined throughout the sampled year; (**b**) Median concentration of BPF determined for each season.

Significant statistical differences for BPA concentrations were found for CD and the other two seasons, while for BPF, non-significant statistical differences were found between HD and CD seasons. Some studies indicate that bisphenols are released into the atmosphere as a consequence of industry emissions and garbage burning, among others [11]. Additionally, during HD season some uncontrolled fires are triggered by relatively high ambient temperatures and dry weather, which promote the release of bisphenols into the atmosphere through volatile particles [21]. On the contrary, during the CD season, relatively high bisphenol concentrations can be due to accumulation, as has been reported for PAH in this region [41], since low solar radiation reduces the rate of photodegradation, which maintains bisphenols in their stable form for longer [64,65].

BPF concentrations had the same order of magnitude in the three seasons, while BPA median concentration in CD was up to one order of magnitude higher than that detected in R and HD. Lower concentrations in the R season can be explained through the bisphenols

Log K_{ow} (BPA = 3.32; BPF = 2.91) [66], which indicates that they can be mostly adsorbed in atmospheric particles and, therefore, deposited during rain events.

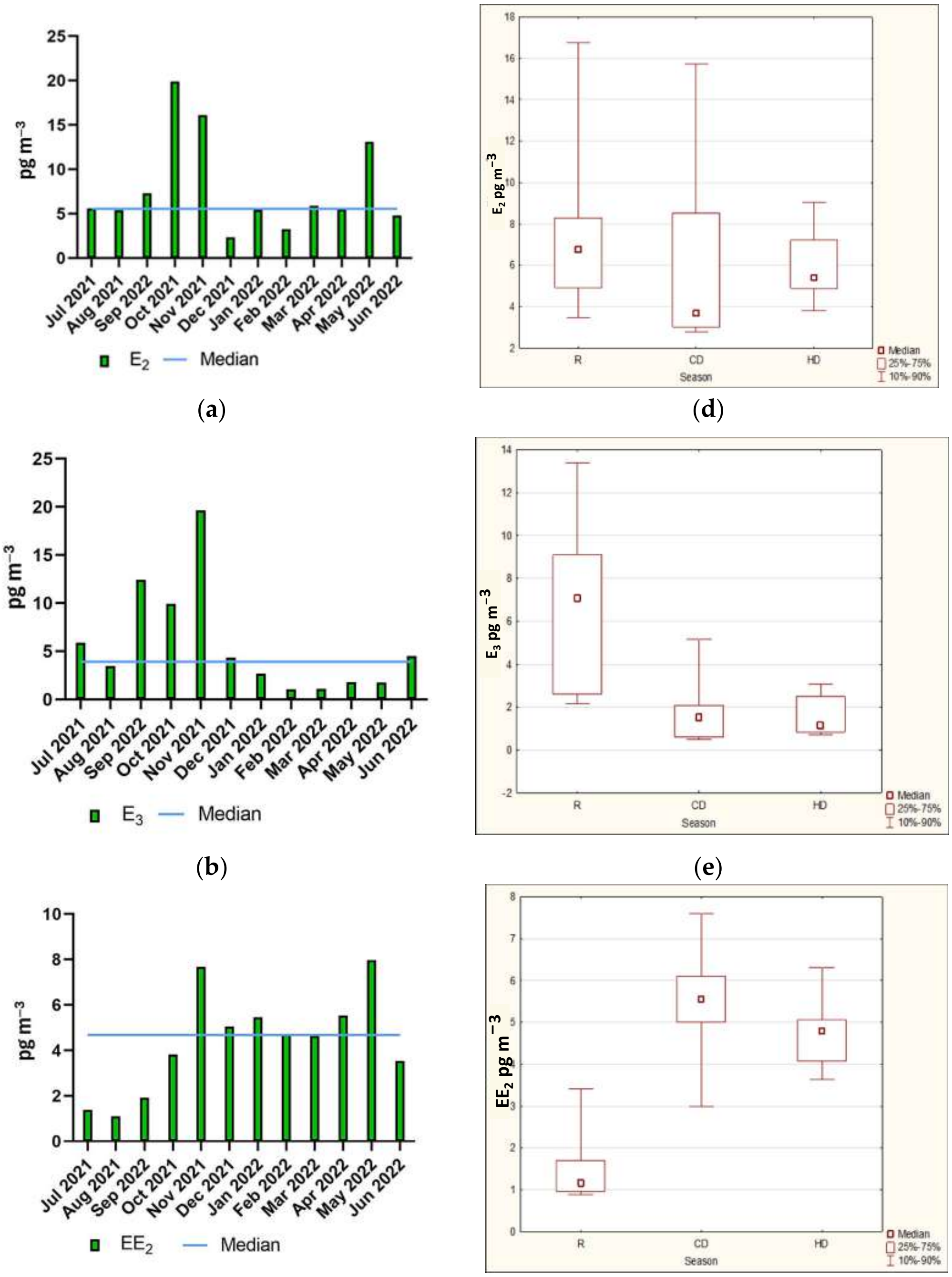
BPA and BPF are used principally in the production of food packages, plastics, and electrical varnishes, among others [67,68], which are important sources of these bisphenols in the atmosphere. The high concentrations of BPA in the CD may be attributed to the practice of burning waste, particularly plastics, for heating during this season. Additionally, industrial production was significantly reduced during 2020 and 2021 due to the COVID-19 pandemic, with operations gradually resuming toward the end of 2021 and early 2022 because of the arrival of components and raw materials from Asia. Other bisphenol sources have been identified in some studies, including combustion processes [69,70], plastic burning areas [11], and domestic waste burns in barrels [71]. Probably, in those events, the BPA remains adsorbed in $PM_{2.5}$, ash particles, or elemental carbon emitted into the atmosphere [65,72] or can be resuspended from soil [12]. BPA has been detected in offices and other workplaces, possibly emitted from household goods or furnishing materials [32,73], as well as near industrial areas [12,65,74].

As a consequence of the USA banning BPA use [75], BPA analogs were introduced to replace it in industrial processes [67,76]. However, the BPA and BPF median concentrations detected in this investigation suggest that BPA is still used more than BPF by Mexico City industries. Studies in animals reported that BPA could have negative health effects [77] and has been demonstrated that it is associated with disrupting functions of the thyroid hormone [78], glucose regulation [79], and bodyweight control [80]. In humans, a relationship has been observed between BPA exposure and cardiometabolic disorders, such as diabetes, hypertension, cardiovascular diseases [75], and endocrine disruption [67]. The European Food Safety Authority has declared that BPA is a carcinogen, particularly in breast cancer development, and its estrogenic activity can reduce sperm count and be toxic to the liver [81].

Nevertheless, it was reported that it is not easy for BPA to enter the human body through the respiratory tract and does not represent a high risk for people's health in comparison to workers involved with the plastic industry [74], who can present high BPA concentrations in blood [75]. Despite this, it is important to continue with BPA and other bisphenols monitoring in the atmosphere to prevent respiratory risks in humans. Additionally, studies in indoor atmospheres revealing similar or higher concentrations than outdoor ones show the need to include BPF in future studies to obtain novel information about its mobility and behavior in the atmosphere [82,83].

Hormones E_2, E_3, and EE_2 were detected in all samples. Annual median concentrations decrease in the order of E_2 (6.22 pg m^{-3}) > EE_2 (4.21 pg m^{-3}) > E_3 (2.60 pg m^{-3}) (Figure 7). The E_2 concentration agrees with that reported by Salgueiro-González et al. in an industrial area in Spain [12].

No meaningful differences were detected for E_2 concentrations among seasons, suggesting a similar behavior in emission concentrations throughout the year. For E_3 and EE_2, significant differences were found between median concentrations of R, CD, and HD seasons. Contrary to alkylphenols and bisphenols, hormones have been detected only in industrial and cattle feed areas [12,84] due to their use as raw material to produce pillows, for hormonal control, and for their use in animals to improve body development. Therefore, principal hormones emission sources toward the atmosphere could be from factories. Despite E_2 has been characterized as the principal endocrine disruptor in humans, studies focused on determining hormone concentrations in the atmosphere are very scarce. Among possible negative human health effects developed by hormones are breast and ovarian cancer in women, prostate and testicular cancer in men, endometriosis, osteoporosis, cardiovascular diseases, cognitive and behavioral alterations, hypertension, and metabolic and immune disorders [85]. So, it is relevant to generate more information about the atmospheric concentrations of this group of compounds.



(**a**) (**d**)

(**b**) (**e**)

(**c**) (**f**)

Figure 7. (**a**–**c**) Concentrations of E_2, E_3, and EE_2, respectively, determined throughout the sampled year; (**d**–**f**) median concentrations of E_2, E_3, and EE_2, respectively, determined for each season.

3.4. Correlations Among Studied Compounds

Commonly, estrogenic compounds studied in this work have different applications in industrial processes for several products, such as plastics (BPA and BPF), cleansing products (4tOP), or pharmaceuticals (E_2, E_3, and EE_2). Although 4NP is not used directly in industrial processes, this is a byproduct of 4tOP degradation. Additionally, other important emission sources are uncontrolled garbage burning, garbage dumps, and e-waste. To identify relationships between the emission sources of these compounds, a Spearman correlation Test ($p \leq 0.05$) was applied, with the purpose of identifying a correlation among determined compounds (Figure 8). Several significant positive correlations were found, suggesting similar emission sources in the atmosphere among the EDCs, 4NP, 4tOP, BPA, BPF, and EE_2, whereas correlation with PAHs were few, only 4NP and BPA with FA, BaA and Chr; in the case of PAH, high molecular PAHs presented high correlations among them with the exception of Ret that is associated to biomass burning, these common sources can be uncontrolled burning garbage, bonfires, industrial and vehicle activities and mechanical transfer from water bodies to atmosphere. Negative correlations are related to degradation processes in the atmosphere, as is the case of E_2, E_3, and Nap.

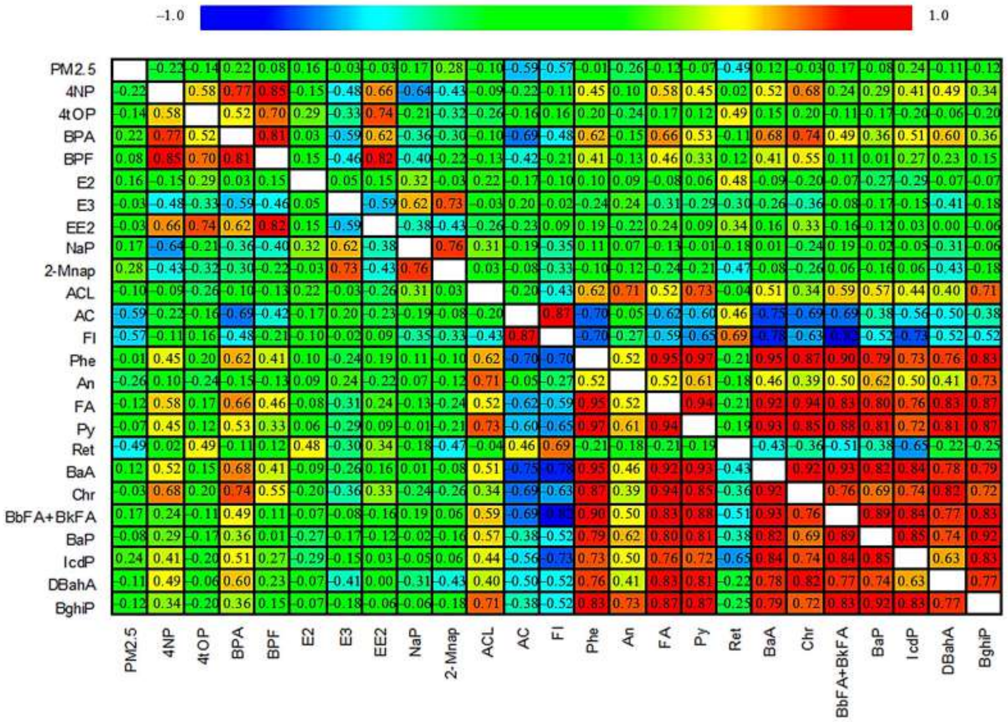


Figure 8. Spearman's correlations determined between EDCs and PAH in the Mexico City atmosphere ($p \leq 0.05$).

3.5. Estrogenic Risk Assessment

Most research related to estrogenic activity has focused on water and sediments developing estrogenicity factors, which could be applied to air studies since the mechanism of estrogen receptor binding and activation is compound-specific and matrix-independent [3]. For the determination of estrogenic risk due to the estrogenic compounds detected in $PM_{2.5}$, EEQ_{E2} was determined as total EEQ_{E2} (ΣEEQ_{E2}) for each season (R, CD, and HD) estimated as the sum of EEQ_{E2} of all compounds (Table 1). The highest EEQ_{E2} value was determined in the R season, while between CD and HD seasons, EEQ_{E2} were similar. Due to their estrogenic level, the hormones group presented the major contribution with around 99% of ΣEEQ_{E2} for all seasons (Table 1). During CD and HD seasons, hormone E_2 contributed more than 80% of estrogenic activity, while E_3 and EE_2 contributed from 5.5 to 22.86% and 2.71 to 8.05%, respectively. In contrast, alkylphenols and bisphenols contributions to the ΣEEQ_{E2} were less than 1% altogether. Although BPA was the compound detected in higher concentrations throughout the year, its EEQ_{E2} contributions were lower because to its low EEF value. Due to the relatively high concentrations of hormones determined in R season, this was the season with major estrogenic activity, with hormones E_2, E_3, and EE_2 as the most important contributors to this risk.

Table 1. Estrogenic activity (EEQ_{E2}) of alkylphenols, bisphenols, and hormones contained $PM_{2.5}$ from an industrial area in Mexico City.

	Season	*n*	**4NP**	**4tOP**	**BPA**	**E_2**	**E_3**	**EE_2**	**ΣEEQ_{E2}**
Seasonal EEQ_{E2} ($ng\ m^{-3}$) [1]	R	8	8.31×10^{-7}	2.12×10^{-5}	5.47×10^{-5}	7.65×10^{-2}	2.35×10^{-2}	2.79×10^{-3}	1.03×10^{-1}
	CD	7	1.96×10^{-6}	1.23×10^{-5}	1.95×10^{-4}	4.93×10^{-2}	3.14×10^{-3}	4.61×10^{-3}	5.73×10^{-2}
	HD	6	1.93×10^{-6}	3.11×10^{-5}	5.88×10^{-5}	6.33×10^{-2}	7.12×10^{-3}	6.03×10^{-3}	7.66×10^{-2}
	ΣEEQ_{E2} (Annual)	21	4.72×10^{-6}	6.46×10^{-5}	3.09×10^{-4}	1.89×10^{-1}	3.38×10^{-2}	1.34×10^{-2}	2.37×10^{-1}
Estrogenicity contribution (%) by season [2]	Season	*n*	4NP	4tOP	BPA	E_2	E_3	EE_2	Total %
	R	8	0.00	0.02	0.05	74.35	22.86	2.71	100.000
	CD	7	0.00	0.02	0.34	86.09	5.49	8.05	100.00
	HD	6	0.00	0.04	0.07	82.71	9.30	7.88	100.00

[1] Estrogenic activity as EEQ_{E2} ($ng\ m^{-3}$) determined for each compound by season; [2] contributions of estrogenic activity by compound by season; *n* = number of samples.

The European Union has established $EEQ_{E2} < 1\ ng\ L^{-1}$ as no estrogenic risk for water bodies, but for air, there is not yet a suggested value. Despite this, it is recommended that studies be performed on these compounds in particles to prevent possible health risks.

According to US-EPA, the long-term exposure inhalation rate proposed in the "Summary Recommended Values for Inhalation", average inhalation volume for children (1–2 years) is 6.8 $m^3\ day^{-1}$, for young people (15–18 years) is 12 $m^3\ day^{-1}$, 17 $m^3\ day^{-1}$ for females and males respectively, and for adults (19–65+ years) is 11.3 and 15.3 $m^3\ day^{-1}$ for females and males, respectively [51]. Thus, according to the inhalation volume, the mean ΣEEQ_{E2} estimated across the year was between 0.07 and 0.17 $ng\ m^{-3}$. It is important to highlight that the values for EEQ_{E2} determined here are only for the six estrogenic analyzed compounds, and the total value of EEQ_{E2} can increase due to the presence of non-studied estrogenic compounds in these samples. Hence, it is important to continue with this kind of study, including a greater number of estrogenic contaminants in future research.

3.6. Polycyclic Aromatic Hydrocarbons

Figure 9 displays the average abundance of PAH during the period of sampling. The total average concentration was 6.68 $ng\ m^{-3}$, where Nap, IcdP, BghiP, 2MNap, and BaP were the most abundant compounds, contributing 80% of the PAH mix. According to the International Agency for Research on Cancer, seven PAH have been classified as possible carcinogens: BaA, Chr, BbFA, BkFA, BaP, IcdP, and DBahA [86]. The annual average concentration of the sum of these PAHs was 3.40 $ng\ m^{-3}$, contributing 52% of total PAHs, which could represent an important risk for the population.

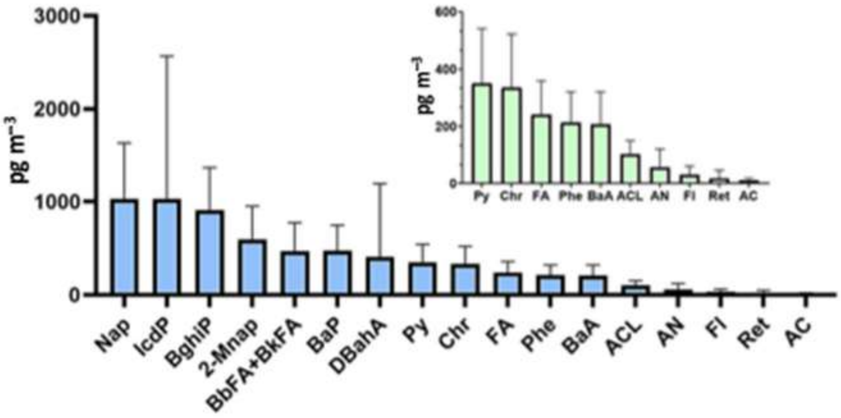
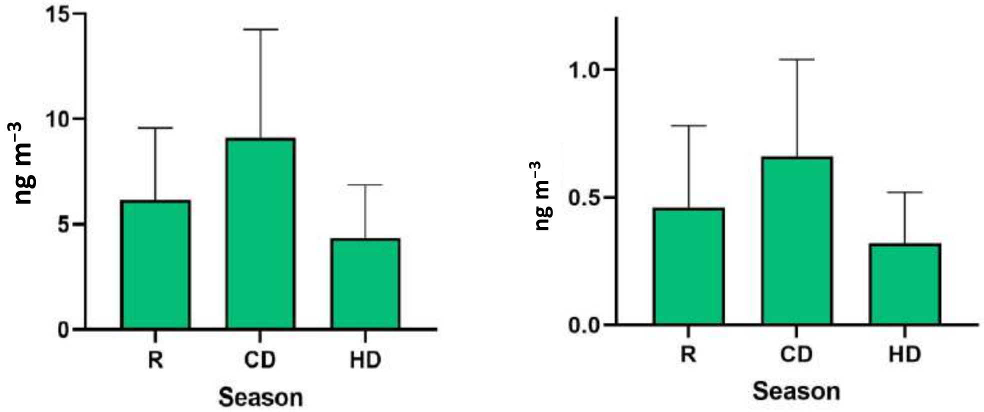


Figure 9. The average concentration of PAH in Mexico City.

The highest ΣPAH concentrations were measured during CD season due to low temperatures, thermal inversions, and stable meteorological conditions, with an average concentration of 9.12 ng m^{-3}, followed by R and HD seasons, with average concentrations of 6.15 ng m^{-3} and 4.35 ng m^{-3}, respectively, whereas BaP concentrations presented the same trend (Figure 10). Significant differences were found between the three seasons in both cases; this behavior of PAH has been reported before in Mexico City but for PM_{10} [41], whereas Amador-Muñoz et al. showed that in the south of Mexico City, PAH concentrations have decreased in the last decades due to the programs implemented by Mexican authorities for the air quality improvement [42].



(**a**) (**b**)

Figure 10. (**a**) Average concentration of ΣPAH determined in seasons; (**b**) Average concentrations of BaP determined during seasons.

Among seasons, significant differences were found between CD and HD for Phe, FA, Py, BaA, Chr, BbFA + BkfA, BaP, IcdP, DbahA, and BghiP and between CD and R for Nap, Phe, FA, Py, BaA, Chr, and IcdP. Meanwhile, between the HD and R seasons, significant differences were found for Nap, FA, BbFA + BkFA, and DBahA. These results indicate that PAH and their source have different behavior during different seasons.

3.7. PAH Health Risk Assessment

The estimated values for the carcinogenic potential of the PAH mixture, as $BaP_{(PEQ)}$, presented a similar carcinogenic risk for all seasons, with an annual average of 0.64. This number is lower than the recommended by the European Union Commission of 1 ng m^{-3} [87] but more than twice the recommended value in Great Britain of 0.25 ng m^{-3}. BaP was the main contributor to carcinogenic risk at 63%, followed by DBahA at 25% and BbF + BKF at 6%. The assessment of mutagenic potential $BaP_{(MEQ)}$ showed values of 0.97, 0.91, and 0.87 ng m^{-3} for HD, CD, and R seasons, respectively. For these mutagenic potential values, BaP is also the main contributor (45%). Policymakers must consider this risk evidence in the establishment of particle control strategies from different sources.

4. Discussion

Despite the actions implemented by the Mexican authorities to reduce $PM_{2.5}$ concentrations, the results show that both Mexican standards and WHO guidelines were exceeded due to extensive activities in the city, such as industrial manufacturing, high traffic, forest fires, and burning garbage from unidentified rural sites, indicating that more actions are required to reduce fine particle concentrations.

Currently, with the exception of PAH, EDC characterization studies in airborne are scarce, even in developed countries. Most are short-term and do not account for the temporal variations in atmospheric concentrations. As in developing countries, the only reported study was conducted in Greece [33]. This research fills a critical gap by developing a methodology for analyzing EDC, providing information on their concentrations, and results for a preliminary risk assessment of endocrine disruptors in $PM_{2.5}$, particularly in Latin America, where no prior studies have been reported.

The differences in EDC concentrations among seasons of alkylphenols, bisphenols, hormones, and PAH indicate that climatic conditions play an important role in the permanence and transport of these compounds. The activities carried out in an industrial area of the city promote the release of those compounds into the atmosphere, where compounds can be transported and inhaled by the population.

In comparison with other studies (Table 2), the average 4tOP concentration detected in this work was 38 times lower than that measured in Tokyo (600 pg m^{-3}) [88] but is similar to that reported in Germany [36]. Still, it is 1.6 times higher than that found in an industrial area in Greece [33] and up to three times higher than that reported in an industrial zone in Spain [12]. Although 4NP is not used directly in industrial processes, it is present in the atmosphere as a consequence of alkylphenol ethoxylates degradation processes, as well as from wastewater treatment emissions, electronic recycling emissions, uncontrolled fires of wastes, and water–air exchange [33]. The average 4NP concentration in this work (0.41 pg m^{-3}) is lower than that of those determined in an industrial area of Greece and in an urban site in Germany [36], although it is higher than that reported for an industrial zone of Spain [12] where 4NP was undetectable in urban, suburban, and industrial sites.

Table 2. Concentration comparison among compounds detected in the atmosphere of Mexico City and other countries.

Compound	**Country**	**Location**	**PM ^{1} (μm)**	**Concentration Range (pg m^{-3})**	**Average (pg m^{-3})**	**Ref.**
4tOP	Mexico	Urban (near industrial area)	2.5	2.56–89.47	15.96	This study
4NP				0.2–1.52	0.41	
BPA				49–2274	649	
BPF				0.88–283.14	24.32	
E_2				2.33–23.06	8.60	
E_3				0.54–21.18	4.90	
EE_2				0.96–7.98	3.93	
4NP	Germany	Urban	---	1.7–117	---	[36]
4tOP				0.3–4.2		
BPA				5–15		
NP	Japan	Urban	---	8500–17,300	12,900	[88]
4tOP				<100–1100	600	
BPA				400–500	450	
BPA	China	Urban	2.5	70–2340	480	[11]
4NP	Greece	Industrial	10	2500–10,900	4960	[33]
4tOP				BDL–20	10	
BPA				BDL–47,300	13,200	
BPF	Korea	Indoor	Dust	n.d.–107 ^{2}	0.50 ^{2}	[82]
4NP	Spain	Industrial	2.5	n.d.	---	[12]
4tOP		Industrial		<24		
BPA		Urban		n.d.–108		
E_2		Industrial		n.d.–<15		
E_3		Industrial		n.d.		
EE_2		Industrial		n.d.		
E_2	USA	Cattle feedyards	2.5	---	0.008 ^{2}	[84]
EE_2					0.026 ^{2}	
BPF	USA	Indoor (Home)	2.5 ^{1}	<LOQ–2220 ^{2}	133 ^{2}	[83]

[1] Aerodynamic diameter of PM; [2] μg g^{-1}; --- not specified; BDL = below detection limit; n.d. = not detected. LOQ = limit of quantification.

Alkylphenol 4tOP range concentration detected in this work is up to three times higher than that detected in an industrial zone from Spain [12] and is similar to that reported in Germany [36]. This study found that BPA median concentration is similar to those determined in China (480 pg m^{-3}) [11] and Japan (500 pg m^{-3}) [88], where BPA source was attributed to several large electronic waste recycling and to urban zones, respectively. Nevertheless, it is two orders of magnitude lower than the BPA average concentration in the atmosphere of an industrial zone of Greece [33] and up to one order of magnitude larger than the concentration range reported in Spain [12]. In the case of BPF, this compound has only been reported in $PM_{2.5}$ of indoor atmospheres in USA houses with one order of magnitude higher than the average BPF concentration determined in this work and in the indoor dust of Korea, with an average concentration of 0.5 µg g^{-1}. In those two studies, BPF was attributed to goods and furniture made by materials containing it [82,83].

The median concentration of E_2 in this work is similar to the study conducted in Spain [12] and around 10 times smaller than that determined on $PM_{2.5}$ from feedyards in the USA [84], considering that in this work, 0.18 ng g^{-1} is equivalent to 8.60 pg m^{-3}.

Regarding the sum of PAH, the median concentration in this work (6.57 ng m^{-3}) is similar to that determined in Spain (6.16 ng m^{-3}), close to an oil refinery, during the COVID-19 pandemic [89]. This concentration is more than three times lower than that reported in Karaj City, Iran (22.55 ng m^{-3}), where the main emission sources identified were a thermal power plant nearby, heavy vehicular traffic, gasoline and vehicular engine emissions, biomass burning, industrial emissions and petrogenic sources [87]. In contrast, the PAH determined in this study is almost 10 times and 37 times lower than concentrations reported in China (60.7 ng m^{-3}) [38] and in the USA (52.8 ng m^{-3}), respectively [90]. In contrast, the average PAH concentration measured in this study is ten times higher than the concentration in Mount Tai in China (0.680 ng m^{-3}), where PAH concentrations were attributed to wood, coal, and biomass combustion, vehicle emissions, and burning of fossil fuels [91].

In Mexico, different studies have been carried out to determine PAH in $PM_{2.5}$. The average PAH concentration found in this study is almost 14 times higher than the average PAH determined in Mexico City (0.48 ng m^{-3}) at the south of the studied point selected herein, where principal PAH emission was associated with light-duty gasoline sources [42], although it is similar to that determined in Guadalajara (5.65 ng m^{-3}), which is another important city of Mexico. In that study, exhaust vehicular traffic was considered the principal emission source of PAH [92]. Nevertheless, the average PAH detected in this study is almost four times smaller than the PAH determined in an adjacent state (Morelos) to Mexico City, where average was between 22.57 and 25.43 ng m^{-3} for two sampled points in Cuernavaca City [93], but only around half the PAH concentration reported for a very recent study in the same city [94], although the carcinogenic potential as BAPeq reported in this last study was four folks higher than that measured in the present study, since in Morelos, atmospheric PAH were related to emissions from gasoline and diesel, coal burning, a sugar mill and biomass burning.

5. Conclusions

Studies in water, soil, and foods have shown that endocrine disruptor compounds that interfere with hormonal systems are commonly found in those media and represent a health risk. Therefore, the study of EDC in the air is crucial because their presence in fine particles adds a significant exposure pathway, since they can enter into the bloodstream after crossing alveolar lung barriers.

To the best of our knowledge, this is the first study not only in Mexico but in Latin America that measured and confirmed the simultaneous presence of several estrogenic semi-volatile compounds contained in atmospheric $PM_{2.5}$. Alkylphenols, bisphenols, and hormones were detected in the atmosphere of Mexico City, with a developed methodology of sampling, extraction, and analyses, which is suitable in terms of precision and accuracy for the quantification of these compounds contained in $PM_{2.5}$ field samples.

This study shows that $PM_{2.5}$ air quality standards and WHO guidelines are frequently exceeded, representing a risk for the population. It was demonstrated that among the species contained in fine particles, the estrogenic compounds in the atmosphere are present in detectable concentrations, some of them higher than in other countries; moreover, the presence of the priority PAH was confirmed.

The median concentration of measured compounds decreased in the following order: ΣPAH > BPA > BPF > 4tOP > E_3 > E_2 > EE_2 > 4NP. Their behavior across the different seasons of the year was determined. The most abundant PAH were Nap > IcdP> BghiP > 2MNap > BaP.

According to the sampled site location, which is near to an industrial area, processing industrial emissions, heavy diesel vehicles, and uncontrolled garbage burning are the main sources of emissions of these compounds into the atmosphere.

Correlations between 0.52 and 0.85 were observed among five of the analyzed EDC: 4NP, 4tOP, BPA, BPF, and E_2, suggesting common sources. Regarding PAH, high molecular weight compounds had a high positive correlation among them, but only Chr, BaA, and FA correlated positively with 4NP and BPA.

The estrogenic risk also showed that hormones are the main contributors to estrogenic activity with 99%, and the carcinogenic potential of PAH of around 0.64 ng m^{-3} was lower than the recommended value of 1 ng m^{-3}. Nevertheless, the obtained values show that there is a risk of exposure to these compounds, and there is not a completely safe value for carcinogenic compounds.

The findings of this study reveal that EDCs are present in the air people breathe, adding to the existing risks of exposure through other environmental pathways. To effectively address this threat, it is crucial to expand research efforts by analyzing a broader range of EDCs in airborne samples and increasing the number of monitoring sites. This will provide a more comprehensive understanding of their spatial distribution, especially in urban and industrial areas where concentrations tend to be higher.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/atmos16020178/s1. Figure S1: Chromatogram obtained for semi-volatile EDCs by GC-dMRM analysis; Table S1: Identification compounds of interest; transitions, collision energies; Table S2: Method validation for studied compounds.

Author Contributions: J.G.R.-L., M.A.M.-T., H.A.S.-N. and V.M.-Á.; Data curation, F.M.-V., B.L.V.-H. and V.M.-Á.; Formal analysis, J.G.R.-L., F.M.-V. and V.M.-Á.; Funding acquisition, V.M.-Á.; Investigation, J.G.R.-L., F.M.-V., M.A.M.-T. and V.M.-Á.; Methodology, J.G.R.-L., M.A.M.-T. and H.A.S.-N.; Project administration, V.M.-Á.; Resources, H.A.S.-N.; Supervision, M.A.M.-T.; Validation, B.L.V.-H.; Visualization, K.L.-V.; Writing—original draft, J.G.R.-L.; Writing—review and editing, K.L.-V. and V.M.-Á. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CONAHCyT, grant number 316642.

Institutional Review Board Statement: The statement is not applicable to studies that do not involve humans or animals.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data of this study can be shared upon request to the authors.

Acknowledgments: JGRL thanks CONAHCyT for the postdoctoral scholarship number 2580933. The authors thank Mario Romero-Romo for the English review of the last version.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ali, M.U.; Liu, G.; Yousaf, B.; Ullah, H.; Abbas, Q.; Munir, M.A.M. A Systematic Review on Global Pollution Status of Particulate Matter-Associated Potential Toxic Elements and Health Perspectives in Urban Environment. *Environ. Geochem. Health* **2019**, *41*, 1131–1162. [CrossRef]
2. Anderson, J.O.; Thundiyil, J.G.; Stolbach, A. Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health. *J. Med. Toxicol.* **2012**, *8*, 166–175. [CrossRef] [PubMed]
3. Darbre, P. Overview of Air Pollution and Endocrine Disorders. *Int. J. Gen. Med.* **2018**, *11*, 191–207. [CrossRef] [PubMed]
4. Wu, W.; Jin, Y.; Carlsten, C. Inflammatory Health Effects of Indoor and Outdoor Particulate Matter. *J. Allergy Clin. Immunol.* **2018**, *141*, 833–844. [CrossRef] [PubMed]
5. Rovelli, S.; Cattaneo, A.; Nischkauer, W.; Borghi, F.; Spinazzè, A.; Keller, M.; Campagnolo, D.; Limbeck, A.; Cavallo, D.M. Toxic Trace Metals in Size-Segregated Fine Particulate Matter: Mass Concentration, Respiratory Deposition, and Risk Assessment. *Environ. Pollut.* **2020**, *266*, 115242. [CrossRef] [PubMed]
6. Millán-Vázquez, F.; Sosa-Echevería, R.; Alarcón-Jiménez, A.L.; Figueroa-Lara, J.D.J.; Torres-Rodríguez, M.; Valle-Hernández, B.L.; Mugica-Álvarez, V. Temporal Variation and Potential Sources of Water-Soluble Inorganic Ions in PM2.5 in Two Sites of Mexico City. *Atmosphere* **2023**, *14*, 1585. [CrossRef]
7. Li, W.; Wang, C.; Shen, H.; Su, S.; Shen, G.; Huang, Y.; Zhang, Y.; Chen, Y.; Chen, H.; Lin, N.; et al. Concentrations and Origins of Nitro-Polycyclic Aromatic Hydrocarbons and Oxy-Polycyclic Aromatic Hydrocarbons in Ambient Air in Urban and Rural Areas in Northern China. *Environ. Pollut.* **2015**, *197*, 156–164. [CrossRef]
8. Verma, V.; Fang, T.; Xu, L.; Peltier, R.E.; Russell, A.G.; Ng, N.L.; Weber, R.J. Organic Aerosols Associated with the Generation of Reactive Oxygen Species (ROS) by Water-Soluble $PM_{2.5}$. *Environ. Sci. Technol.* **2015**, *49*, 4646–4656. [CrossRef] [PubMed]
9. Gea, M.; Fea, E.; Racca, L.; Gilli, G.; Gardois, P.; Schilirò, T. Atmospheric Endocrine Disruptors: A Systematic Review on Oestrogenic and Androgenic Activity of Particulate Matter. *Chemosphere* **2024**, *349*, 140887. [CrossRef]
10. US-EPA Environmental Protection Agency. Overview of Endocrine Disruption. Available online: https://www.epa.gov/endocrine-disruption/overview-endocrine-disruption (accessed on 5 February 2024).
11. Fu, P.; Kawamura, K. Ubiquity of Bisphenol A in the Atmosphere. *Environ. Pollut.* **2010**, *158*, 3138–3143. [CrossRef]
12. Salgueiro-González, N.; López De Alda, M.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D.; Barceló, D. Determination of 13 Estrogenic Endocrine Disrupting Compounds in Atmospheric Particulate Matter by Pressurised Liquid Extraction and Liquid Chromatography-Tandem Mass Spectrometry. *Anal. Bioanal. Chem.* **2013**, *405*, 8913–8923. [CrossRef] [PubMed]
13. Yang, L.; Zhang, H.; Zhang, X.; Xing, W.; Wang, Y.; Bai, P.; Tang, N. Exposure to Atmospheric Particulate Matter-Bound Polycyclic Aromatic Hydrocarbons and Their Health Effects: A Review. *Int. J. Environ. Res. Public Health* **2021**, *18*, 2177. [CrossRef] [PubMed]
14. da Souza, T.L.d; sa Luz, J.Z.; de Almeida Roque, A.; Opuskevitch, I.; da Silva Ferreira, F.C.A.; de Oliveira Ribeiro, C.A.; Neto, F.F. Exploring the Endocrine Disrupting Potential of a Complex Mixture of PAHs in the Estrogen Pathway in Oreochromis Niloticus Hepatocytes. *Aquat. Toxicol.* **2024**, *273*, 107002. [CrossRef] [PubMed]
15. Calderón-Moreno, G.M.; Vergara-Sánchez, J.; Saldarriaga-Noreña, H.; García-Betancourt, M.L.; Domínguez-Patiño, M.L.; Moeller-Chávez, G.E.; Ronderos-Lara, J.G.; Arias-Montoya, M.I.; Montoya-Balbas, I.J.; Murillo-Tovar, M.A. Occurrence and Risk Assessment of Steroidal Hormones and Phenolic Endocrine Disrupting Compounds in Surface Water in Cuautla River, Mexico. *Water* **2019**, *11*, 2628. [CrossRef]
16. Peremiquel-Trillas, P.; Benavente, Y.; Martín-Bustamante, M.; Casabonne, D.; Pérez-Gómez, B.; Gómez-Acebo, I.; Oliete-Canela, A.; Diéguez-Rodríguez, M.; Tusquets, I.; Amiano, P.; et al. Alkylphenolic Compounds and Risk of Breast and Prostate Cancer in the MCC-Spain Study. *Environ. Int.* **2019**, *122*, 389–399. [CrossRef] [PubMed]
17. In, S.-J.; Kim, S.-H.; Go, R.-E.; Hwang, K.-A.; Choi, K.-C. Benzophenone-1 and Nonylphenol Stimulated MCF-7 Breast Cancer Growth by Regulating Cell Cycle and Metastasis-Related Genes Via an Estrogen Receptor α-Dependent Pathway. *J. Toxicol. Environ. Health Part A* **2015**, *78*, 492–505. [CrossRef] [PubMed]
18. Vivacqua, A.; Recchia, A.G.; Fasanella, G.; Gabriele, S.; Carpino, A.; Rago, V.; Gioia, M.L.D.; Leggio, A.; Bonofiglio, D.; Liguori, A.; et al. The Food Contaminants Bisphenol A and 4-Nonylphenol Act as Agonists for Estrogen Receptor in MCF7 Breast Cancer Cells. *Endocrine* **2003**, *22*, 275–284. [CrossRef] [PubMed]
19. Montano, L.; Pironti, C.; Pinto, G.; Ricciardi, M.; Buono, A.; Brogna, C.; Venier, M.; Piscopo, M.; Amoresano, A.; Motta, O. Polychlorinated Biphenyls (PCBs) in the Environment: Occupational and Exposure Events, Effects on Human Health and Fertility. *Toxics* **2022**, *10*, 365. [CrossRef]

20. Vom Saal, F.S.; Vandenberg, L.N. Update on the Health Effects of Bisphenol A: Overwhelming Evidence of Harm. *Endocrinology* **2021**, *162*, bqaa171. [CrossRef]
21. Abraham, A.; Chakraborty, P. A Review on Sources and Health Impacts of Bisphenol A. *Rev. Environ. Health* **2020**, *35*, 201–210. [CrossRef]
22. Farrugia, F.; Aquilina, A.; Vassallo, J.; Pace, N.P. Bisphenol A and Type 2 Diabetes Mellitus: A Review of Epidemiologic, Functional, and Early Life Factors. *Int. J. Environ. Res. Public Health* **2021**, *18*, 716. [CrossRef]
23. Rahman, M.S.; Kwon, W.-S.; Lee, J.-S.; Yoon, S.-J.; Ryu, B.-Y.; Pang, M.-G. Bisphenol-A Affects Male Fertility via Fertility-Related Proteins in Spermatozoa. *Sci. Rep.* **2015**, *5*, 9169. [CrossRef]
24. Moore, S.C.; Matthews, C.E.; Ou Shu, X.; Yu, K.; Gail, M.H.; Xu, X.; Ji, B.-T.; Chow, W.-H.; Cai, Q.; Li, H.; et al. Endogenous Estrogens, Estrogen Metabolites, and Breast Cancer Risk in Postmenopausal Chinese Women. *J. Natl. Cancer Inst.* **2016**, *108*, djw103. [CrossRef]
25. Nelles, J.L.; Hu, W.-Y.; Prins, G.S. Estrogen Action and Prostate Cancer. *Expert Rev. Endocrinol. Metab.* **2011**, *6*, 437–451. [CrossRef] [PubMed]
26. Kolok, A.S.; Ali, J.M.; Rogan, E.G.; Bartelt-Hunt, S.L. The Fate of Synthetic and Endogenous Hormones Used in the US Beef and Dairy Industries and the Potential for Human Exposure. *Curr. Environ. Health Rep.* **2018**, *5*, 225–232. [CrossRef]
27. Kabuto, M.; Akiba, S.; Stevens, R.G.; Neriishi, K.; Land, C.E. A Prospective Study of Estradiol and Breast Cancer in Japanese Women. *Cancer Epidemiol. Biomark. Prev.* **2000**, *9*, 575–579.
28. Barańska, A.; Kanadys, W. Oral Contraceptive Use and Breast Cancer Risk for BRCA1 and BRCA2 Mutation Carriers: Systematic Review and Meta-Analysis of Case–Control Studies. *Cancers* **2022**, *14*, 4774. [CrossRef] [PubMed]
29. Narod, S.A. Oral Contraceptives and the Risk of Breast Cancer in BRCA1 and BRCA2 Mutation Carriers. *J. Natl. Cancer Inst.* **2002**, *94*, 1773–1779. [CrossRef]
30. Stanczyk, F.Z.; Archer, D.F.; Bhavnani, B.R. Ethinyl Estradiol and 17β-Estradiol in Combined Oral Contraceptives: Pharmacokinetics, Pharmacodynamics and Risk Assessment. *Contraception* **2013**, *87*, 706–727. [CrossRef]
31. Zhang, Y.; Dong, S.; Wang, H.; Tao, S.; Kiyama, R. Biological Impact of Environmental Polycyclic Aromatic Hydrocarbons (ePAHs) as Endocrine Disruptors. *Environ. Pollut* **2016**, *213*, 809–824. [CrossRef] [PubMed]
32. Wilson, N.K.; Chuang, J.C.; Lyu, C. Levels of Persistent Organic Pollutants in Several Child Day Care Centers. *J. Expo. Sci. Environ. Epidemiol.* **2001**, *11*, 449–458. [CrossRef]
33. Salapasidou, M.; Samara, C.; Voutsa, D. Endocrine Disrupting Compounds in the Atmosphere of the Urban Area of Thessaloniki, Greece. *Atmos. Environ.* **2011**, *45*, 3720–3729. [CrossRef]
34. Saito, I.; Onuki, A.; Seto, H. Indoor Air Pollution by Alkylphenols in Tokyo. *Indoor Air* **2004**, *14*, 325–332. [CrossRef]
35. Becouze, C.; Wiest, L.; Baudot, R.; Bertrand-Krajewski, J.-L.; Cren-Olivé, C. Optimisation of Pressurised Liquid Extraction for the Ultra-Trace Quantification of 20 Priority Substances from the European Water Framework Directive in Atmospheric Particles by GC–MS and LC–FLD–MS/MS. *Anal. Chim. Acta* **2011**, *693*, 47–53. [CrossRef] [PubMed]
36. Berkner, S.; Streck, G.; Herrmann, R. Development and Validation of a Method for Determination of Trace Levels of Alkylphenols and Bisphenol A in Atmospheric Samples. *Chemosphere* **2004**, *54*, 575–584. [CrossRef] [PubMed]
37. Carreras, H.A.; Calderón-Segura, M.E.; Gómez-Arroyo, S.; Murillo-Tovar, M.A.; Amador-Muñoz, O. Composition and Mutagenicity of PAHs Associated with Urban Airborne Particles in Córdoba, Argentina. *Environ. Pollut.* **2013**, *178*, 403–410. [CrossRef] [PubMed]
38. Ma, W.-L.; Zhu, F.-J.; Liu, L.-Y.; Jia, H.-L.; Yang, M.; Li, Y.-F. PAHs in Chinese Atmosphere: Gas/Particle Partitioning. *Sci. Total Environ.* **2019**, *693*, 133623. [CrossRef]
39. Nayak, Y.; Chakradhari, S.; Patel, K.S.; Patel, R.K.; Yurdakul, S.; Saathoff, S.; Pablo, M.R. Distribution, variations, fate and sources of polycyclic aromatic hydrocarbons and carbon in particulate matter, road dust, and sediments in Central India. *Polycyclic Aromat. Compd.* **2023**, 1309–1331. [CrossRef]
40. Villanueva, F.; Tapia, A.; Cabañas, B.; Martínez, E.; Albaladejo, J. Characterization of Particulate Polycyclic Aromatic Hydrocarbons in an Urban Atmosphere of Central-Southern Spain. *Environ. Sci. Pollut. Res.* **2015**, *22*, 18814–18823. [CrossRef] [PubMed]
41. Mugica, V.; Hernández, S.; Torres, M.; García, R. Seasonal Variation of Polycyclic Aromatic Hydrocarbon Exposure Levels in Mexico City. *J. Air Waste Manag. Assoc.* **2010**, *60*, 548–555. [CrossRef]
42. Amador-Muñoz, O.; Martínez-Domínguez, Y.M.; Gómez-Arroyo, S.; Peralta, O. Current Situation of Polycyclic Aromatic Hydrocarbons (PAH) in PM2.5 in a Receptor Site in Mexico City and Estimation of Carcinogenic PAH by Combining Non-Real-Time and Real-Time Measurement Techniques. *Sci. Total Environ.* **2020**, *703*, 134526. [CrossRef]
43. Instituto Nacional de Estadística y Geografía (INEGI) México En Cifras. Available online: https://www.inegi.org.mx/app/areasgeograficas/?ag=07000009#collapse-Resumen (accessed on 5 February 2024).
44. Instituto Nacional de Estadística y Geografía (INEGI) Conjunto de Datos: Vehículos de Motor Registrados En Circulación. Available online: https://www.inegi.org.mx/sistemas/olap/Proyectos/bd/continuas/transporte/vehiculos.asp?s=est?c=13158 (accessed on 5 February 2024).

45. SENASICA Padrón de Establecimientos Industriales y Mercantiles de Productos Veterinarios. Available online: https://datos.gob.mx/busca/dataset/padron-de-establecimientos-industriales-y-mercantiles-de-productos-veterinarios (accessed on 5 February 2024).
46. Municipios.mx Azcapotzalco. Available online: http://www.municipios.mx/distrito-federal/azcapotzalco/ (accessed on 5 February 2024).
47. US-EPA Ambient Air Sampling SESDPROC-303-R5. Available online: https://www.epa.gov/system/files/documents/2022-06/Ambient%20Air%20Sampling(SESDPROC-303-R5)_0.pdf (accessed on 25 December 2024).
48. Ronderos-Lara, J.G.; Saldarriaga-Noreña, H.; Murillo-Tovar, M.A.; Alvarez, L.; Vergara-Sánchez, J.; Barba, V.; Guerrero-Alvarez, J.A. Distribution and Estrogenic Risk of Alkylphenolic Compounds, Hormones and Drugs Contained in Water and Natural Surface Sediments, Morelos, Mexico. *Separations* **2022**, *9*, 19. [CrossRef]
49. Valle-Hernández, B.L.; Mugica-Álvarez, V.; Salinas-Talavera, E.; Amador-Muñoz, O.; Murillo-Tovar, M.A.; Villalobos-Pietrini, R.; De Vizcaya-Ruíz, A. Temporal Variation of Nitro-Polycyclic Aromatic Hydrocarbons in PM10 and PM2.5 Collected in Northern Mexico City. *Sci. Total Environ.* **2010**, *408*, 5429–5438. [CrossRef] [PubMed]
50. Céspedes, R.; Petrovic, M.; Raldúa, D.; Saura, Ú.; Piña, B.; Lacorte, S.; Viana, P.; Damià, B. Integrated Procedure for Determination of Endocrine-Disrupting Activity in Surface Waters and Sediments by Use of the Biological Technique Recombinant Yeast Assay and Chemical Analysis by LC-ESI-MS. *Anal. Bioanal. Chem.* **2004**, *378*, 697–708. [CrossRef] [PubMed]
51. US-EPA Exposure Factors Handbook. Available online: https://www.epa.gov/expobox/about-exposure-factors-handbook (accessed on 25 December 2024).
52. Durant, J.L.; Busby, W.F.; Lafleur, A.L.; Penman, B.W.; Crespi, C.L. Human Cell Mutagenicity of Oxygenated, Nitrated and Unsubstituted Polycyclic Aromatic Hydrocarbons Associated with Urban Aerosols. *Mutat. Res./Genet. Toxicol.* **1996**, *371*, 123–157. [CrossRef] [PubMed]
53. Nisbet, I.C.T.; LaGoy, P.K. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* **1992**, *16*, 290–300. [CrossRef] [PubMed]
54. US-EPA SW-846 Test Method 8000D: Determinative Chromatographic Separations. Available online: https://www.epa.gov/hw-sw846/sw-846-test-method-8000d-determinative-chromatographic-separations (accessed on 4 September 2024).
55. World Health Organization. WHO Global Guidelines on Air Quality: Suspended Particles (PM2.5 and PM10), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide. Summary [WHO Global Air Quality Guidelines: Particulate Matter (PM2.5 and PM10), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide. Available online: https://www.who.int/publications/i/item/9789240034228 (accessed on 21 July 2024).
56. Warhurst, A.M. An Environmental Assessment of Alkylphenol Ethoxylates and Alkylphenols. Available online: https://www.researchgate.net/publication/270362760_An_Environmental_Assessment_of_Alkylphenol_Ethoxylates_and_Alkylphenols (accessed on 31 January 2025).
57. Dachs, J.; Van Ry, D.A.; Eisenreich, S.J. Occurrence of Estrogenic Nonylphenols in the Urban and Coastal Atmosphere of the Lower Hudson River Estuary. *Environ. Sci. Technol.* **1999**, *33*, 2676–2679. [CrossRef]
58. Fries, E.; Puttmann, W. Ocurrence of 4-Nonylphenol in Rain and Snow. *Atmos. Environ.* **2004**, *38*, 2013–2016. [CrossRef]
59. Cox Caroline Nonyl Phenol and Related Chemicals. Available online: https://www.cabidigitallibrary.org/doi/full/10.5555/19960504349 (accessed on 27 September 2024).
60. US-EPA Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan [RIN 2070-ZA09]. Available online: https://www.epa.gov/sites/default/files/2015-09/documents/rin2070-za09_np-npes_action_plan_final_2010-08-09.pdf (accessed on 21 July 2024).
61. Bergé, A.; Cladière, M.; Gasperi, J.; Coursimault, A.; Tassin, B.; Moilleron, R. Meta-Analysis of Environmental Contamination by Alkylphenols. *Environ. Sci. Pollut. Res.* **2012**, *19*, 3798–3819. [CrossRef] [PubMed]
62. Alothman, Z.A.; Badjah, A.Y.; Ali, I. Facile Synthesis and Characterization of Multi Walled Carbon Nanotubes for Fast and Effective Removal of 4-tert-octylphenol Endocrine Disruptor in Water. *J. Mol. Liq.* **2019**, *275*, 41–48. [CrossRef]
63. Van Ry, D.A.; Dachs, J.; Gigliotti, C.L.; Brunciak, P.A.; Nelson, E.D.; Eisenreich, S.J. Atmospheric Seasonal Trends and Environmental Fate of Alkylphenols in the Lower Hudson River Estuary. *Environ. Sci. Technol.* **2000**, *34*, 2410–2417. [CrossRef]
64. Cecinato, A.; Romagnoli, P.; Perilli, M.; Balducci, C. Nonylphenol and Bisphenol A in Ambient Particulates: A Preliminary Approach in Italy. *Environ. Toxicol. Stud. J.* **2017**, *1*, 3. Available online: https://www.imedpub.com/articles/nonylphenol-and-bisphenol-a-in-ambientparticulates-a-preliminary-approach-in-italy.php?aid=21159 (accessed on 29 January 2025).
65. Graziani, N.S.; Carreras, H.; Wannaz, E. Atmospheric Levels of BPA Associated with Particulate Matter in an Urban Environment. *Heliyon* **2019**, *5*, e01419. [CrossRef]
66. PubChem National Library of Medicine, National Center for Biotechnology Information. Available online: https://pubchem.ncbi.nlm.nih.gov/ (accessed on 2 October 2024).
67. Rochester, J.R.; Bolden, A.L. Bisphenol S and F: A Systematic Review and Comparison of the Hormonal Activity of Bisphenol A Substitutes. *Environ. Health Perspect.* **2015**, *123*, 643–650. [CrossRef] [PubMed]
68. Usman, A.; Ikhlas, S.; Ahmad, M. Occurrence, Toxicity and Endocrine Disrupting Potential of Bisphenol-B and Bisphenol-F: A Mini-Review. *Toxicol. Lett.* **2019**, *312*, 222–227. [CrossRef] [PubMed]

69. Huang, Y.Q.; Wong, C.K.C.; Zheng, J.S.; Bouwman, H.; Barra, R.; Wahlström, B.; Neretin, L.; Wong, M.H. Bisphenol A (BPA) in China: A Review of Sources, Environmental Levels, and Potential Human Health Impacts. *Environ. Int.* **2012**, *42*, 91–99. [CrossRef] [PubMed]
70. Peltonen, K.; Pukkila, J. Determination of Bisphenol A in Air by High-Performance Liquid Chromatography with Electrochemical Detection. *J. Chromatogr. A* **1988**, *439*, 375–380. [CrossRef] [PubMed]
71. Sidhu, S.; Gullett, B.; Striebich, R.; Klosterman, J.; Contreras, J.; DeVito, M. Endocrine Disrupting Chemical Emissions from Combustion Sources: Diesel Particulate Emissions and Domestic Waste Open Burn Emissions. *Atmos. Environ.* **2005**, *39*, 801–811. [CrossRef]
72. Simoneit, B.R.T.; Medeiros, P.M.; Didyk, B.M. Combustion Products of Plastics as Indicators for Refuse Burning in the Atmosphere. *Environ. Sci. Technol.* **2005**, *39*, 6961–6970. [CrossRef] [PubMed]
73. Alliot, F.; Moreau-Guigon, E.; Bourges, C.; Desportes, A.; Teil, M.-J.; Blanchard, M.; Chevreuil, M. A Multi-Residue Method for Characterization of Endocrine Disruptors in Gaseous and Particulate Phases of Ambient Air. *Atmos. Environ.* **2014**, *92*, 1–8. [CrossRef]
74. Jiao, Z.; Guo, Z.; Zhang, S.; Chen, H.; Xie, H.; Zeng, S. Novel Extraction for Endocrine Disruptors in Atmospheric Particulate Matter. *Anal. Lett.* **2015**, *48*, 1355–1366. [CrossRef]
75. Bao, W.; Liu, B.; Rong, S.; Dai, S.Y.; Trasande, L.; Lehmler, H.-J. Association Between Bisphenol A Exposure and Risk of All-Cause and Cause-Specific Mortality in US Adults. *JAMA Netw. Open* **2020**, *3*, e2011620. [CrossRef]
76. Lehmler, H.-J.; Liu, B.; Gadogbe, M.; Bao, W. Exposure to Bisphenol A, Bisphenol F, and Bisphenol S in U.S. Adults and Children: The National Health and Nutrition Examination Survey 2013–2014. *ACS Omega* **2018**, *3*, 6523–6532. [CrossRef]
77. Rubin, B.S.; Soto, A.M. Bisphenol A: Perinatal Exposure and Body Weight. *Mol. Cell. Endocrinol.* **2009**, *304*, 55–62. [CrossRef]
78. Moriyama, K.; Tagami, T.; Akamizu, T.; Usui, T.; Saijo, M.; Kanamoto, N.; Hataya, Y.; Shimatsu, A.; Kuzuya, H.; Nakao, K. Thyroid Hormone Action Is Disrupted by Bisphenol A as an Antagonist. *J. Clin. Endocrinol. Metab.* **2002**, *87*, 5185–5190. [CrossRef]
79. Ropero, A.B.; Alonso-Magdalena, P.; García-García, E.; Ripoll, C.; Fuentes, E.; Nadal, A. Bisphenol-A Disruption of the Endocrine Pancreas and Blood Glucose Homeostasis. *Int. J. Androl.* **2008**, *31*, 194–200. [CrossRef]
80. Rubin, B.S.; Murray, M.K.; Damassa, D.A.; King, J.C.; Soto, A.M. Perinatal Exposure to Low Doses of Bisphenol A Affects Body Weight, Patterns of Estrous Cyclicity, and Plasma LH Levels. *Environ. Health Perspect.* **2001**, *109*, 675–680. [CrossRef]
81. European Food Safety Authority, EFSA Opinion of the Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food (AFC) Related to 2,2-BIS(4-HYDROXYPHENYL)PROPANE. Available online: https://data.europa.eu/doi/10.2903/j.efsa.2007.428 (accessed on 21 July 2024).
82. Liao, C.; Liu, F.; Guo, Y.; Moon, H.-B.; Nakata, H.; Wu, Q.; Kannan, K. Occurrence of Eight Bisphenol Analogues in Indoor Dust from the United States and Several Asian Countries: Implications for Human Exposure. *Environ. Sci. Technol.* **2012**, *46*, 9138–9145. [CrossRef]
83. Xue, J.; Wan, Y.; Kannan, K. Occurrence of Bisphenols, Bisphenol A Diglycidyl Ethers (BADGEs), and Novolac Glycidyl Ethers (NOGEs) in Indoor Air from Albany, New York, USA, and Its Implications for Inhalation Exposure. *Chemosphere* **2016**, *151*, 1–8. [CrossRef]
84. Blackwell, B.R.; Wooten, K.J.; Buser, M.D.; Johnson, B.J.; Cobb, G.P.; Smith, P.N. Occurrence and Characterization of Steroid Growth Promoters Associated with Particulate Matter Originating from Beef Cattle Feedyards. *Environ. Sci. Technol.* **2015**, *49*, 8796–8803. [CrossRef]
85. Yazdan, M.; Kumar, R.; Leung, S.W. The Environmental and Health Impacts of Steroids and Hormones in Wastewater Effluent, as Well as Existing Removal Technologies: A Review. *Ecologies* **2022**, *3*, 206–224. [CrossRef]
86. IARC Chemical Agents and Related Occupations IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Available online: https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Chemical-Agents-And-Related-Occupations-2012 (accessed on 25 December 2024).
87. Azimi-Yancheshmeh, R.; Moeinaddini, M.; Feiznia, S.; Riyahi-Bakhtiari, A.; Savabieasfahani, M.; Van Hullebusch, E.D.; Asgari Lajayer, B. Seasonal and Spatial Variations in Atmospheric PM2.5-Bound PAHs in Karaj City, Iran: Sources, Distributions, and Health Risks. *Sustain. Cities Soc.* **2021**, *72*, 103020. [CrossRef]
88. Inoue, K.; Yoshida, S.; Nakayama, S.; Ito, R.; Okanouchi, N.; Nakazawa, H. Development of Stable Isotope Dilution Quantification Liquid Chromatography–Mass Spectrometry Method for Estimation of Exposure Levels of Bisphenol A, 4-Tert-Octylphenol, 4-Nonylphenol, Tetrabromobisphenol A, and Pentachlorophenol in Indoor Air. *Arch. Environ. Contam. Toxicol.* **2006**, *51*, 503–508. [CrossRef]
89. Guzmán, M.A.; Fernández, A.J.; Boente, C.; Márquez, G.; Sánchez De La Campa, A.M.; Lorenzo, E. Study of PM2.5-Bound Polycyclic Aromatic Hydrocarbons and Anhydro-Sugars in Ambient Air near Two Spanish Oil Refineries: COVID-19 Effects. *Atmos. Pollut. Res.* **2023**, *14*, 101694. [CrossRef]
90. Jia, C.; Xue, Z.; Fu, X.; Sultana, F.; Smith, L.J.; Zhang, Y.; Li, Y.; Liu, B. Impacts of Independence Day Fireworks on Pollution Levels of Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in the U.S. *Sci. Total Environ.* **2020**, *743*, 140774. [CrossRef]

91. Zhen, Z.; Yin, Y.; Chen, K.; Zhen, X.; Zhang, X.; Jiang, H.; Wang, H.; Kuang, X.; Cui, Y.; Dai, M.; et al. Concentration and Atmospheric Transport of PM2.5-Bound Polycyclic Aromatic Hydrocarbons at Mount Tai, China. *Sci. Total Environ.* **2021**, *786*, 147513. [CrossRef]
92. Murillo-Tovar, M.A.; Barradas-Gimate, A.; Arias-Montoya, M.I.; Saldarriaga-Noreña, H.A. Polycyclic Aromatic Hydrocarbons (PAHs) Associated with PM2.5 in Guadalajara, Mexico: Environmental Levels, Health Risks and Possible Sources. *Environments* **2018**, *5*, 62. [CrossRef]
93. Saldarriaga-Noreña, H.; López-Márquez, R.; Murillo-Tovar, M.; Hernández-Mena, L.; Ospina-Noreña, E.; Sánchez-Salinas, E.; Waliszewski, S.; Montiel-Palma, S. Analysis of PAHs Associated with Particulate Matter PM2.5 in Two Places at the City of Cuernavaca, Morelos, México. *Atmosphere* **2015**, *6*, 1259–1270. [CrossRef]
94. Valle-Hernández, B.L.; Figueroa-Lara, J.D.J.; Torres-Rodríguez, M.; Ginéz-Hernández, N.; Álvarez-Lupercio, T.; Mugica-Álvarez, V. Levels, Sources and Risk Assessment of Carbonaceous and Organic Species Associated with PM2.5 in Two Small Cities of Morelos, Mexico. *Atmosphere* **2024**, *15*, 1496. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.