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A Brief Review on Emerging Indoor Chemical Pollutants

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Abstract: Recently, there has been increased concern about emerging pollutants (EPs). Many EPs can be found in consumer products and are regarded as primary indoor contaminants. This review paper focuses on the overview of some emerging indoor chemical pollutants, their negative health effects, appropriate sampling methods, drawbacks associated with them, and the analytical techniques used. Some of the challenges identified during this review included the ease of access to affordable sampling equipment and analytical instruments. More sensitive and cost-effective sampling and analytical equipment should be made available to allow for continuous monitoring of these emerging pollutants, especially in low and middle-income countries.

Keywords: Emerging indoor chemical pollutants, Air sampling methodology; Indoor air quality; Human exposure

1. Introduction.

Air pollution is one of the principal causes of diseases and death today [1-3]. Indoor and outdoor environmental quality have a gross impact on the overall well-being of living organisms [4]. It is worthy of note that the extent of human exposure to contaminants from diverse indoor and outdoor sources can be significantly influenced by the nature of the building, its purpose, and its unique characteristics such as age and maintenance [5].

Incessant and ever-growing industrialization, urbanization, and the invention of new consumables have resulted in the emergence of new pollutants in a variety of forms and types that are challenging to detect and analyze due to their unique characteristics and complex source points [6-7]. These pollutants are known as emerging pollutants (EPs), and the list is endless due to humans' endless quest for new products. Emerging pollutants are defined differently by different authors and regulatory bodies. However, in the context of this review paper, emerging pollutants are defined as natural or synthetic substances or mixtures that have been identified as a potential threat to the ecosystem's overall well-being. There is a need for acceptance criteria, international standards, and regulations, adequate toxicological and morphological information, as well as data in regards to their emission rates and detection limits. This is because of the adverse effects these chemicals can have on human physiology [8-9].

Typical examples of these emerging pollutants are pharmaceuticals, cosmetics and skin-care products, pesticides, herbicides, germicides, surfactants, endocrine disrupting compounds (EDCs), and chemical effluent discharge [10]. In addition, some of the emerging chemical pollutants include polychlorinated biphenyls, polybrominated diphenyl ethers, brominated flame retardants, phthalate esters, hexabromocyclododecane, perfluorocarbon, UV-filter, synthetic musk, paraben, formaldehyde, butadiene, siloxane, neonicotinoids, drug residue, and some transition metals such as arsenium and vanadium [7, 11]. There are several unknown and unidentified air pollutants present in the various environmental matrices because of incomplete combustion from different point sources. Many chemical reactions in an indoor environment trigger indoor air pollutants. Ephemeral radicals such as hydroxyl groups (-OH), hydroperoxy (HO₂), organic peroxy, nitrate (NO₃) radical, and the formation of volatile organic compounds such as formaldehyde and acrolein, which are strong airway irritants produced by the reaction between terpenes and ozone, are some of the sources of reactive chemicals in an indoor environment [12-13].



Indoor air pollution can occur via a variety of routes, including dermal, inhalation, and direct and indirect ingestion [14]. The adverse health effects of these EPs can be short-term or long-term depending on the depth of exposure. Some of the adverse health effects are headaches, dizziness, nausea, allergy attacks, respiratory problems, asthma, neurological deficiency outcomes, and cancer [15]. This review paper gives a brief overview of the emerging indoor chemical pollutants in the air, their negative effects on human health, appropriate sampling and instrumental analysis methodologies, and their associated drawbacks.

1.1 A brief highlight on selected emerging indoor chemical pollutants and their mechanisms of exerting adverse health effects.

1.1.1. *Polychlorinated biphenyls (PCBs)* have been in use since the 20th century for industrial purposes. Their physical and chemical properties provide a wide array of industrial applications. They are man-made organic chemicals that are toxic to both humans and the environment. Their high affinity for organic materials allows for bioaccumulation within the food chain, such that when food products that have been exposed to PCBs are consumed, it triggers some serious health concerns [16].

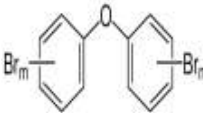
1.1.2. *Polybrominated diphenyl ethers (PBDEs)* are chemical compounds that are covalently bonded to polymeric products, such as epoxy glue, plastic bags, and polymer-based paints, to increase their ignition resistance. Consequently, they can percolate into the environment where such materials are in use and cause a series of mild to major health concerns [17].

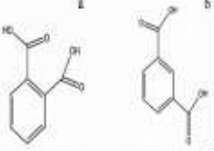
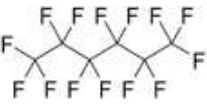
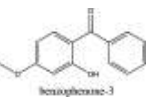
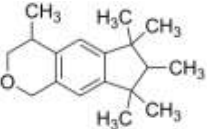
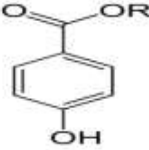
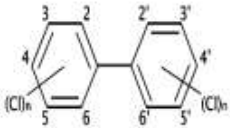
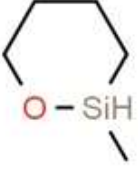
1.1.3. *Phthalic acid esters (PAEs)* are plasticizers that are commonly bonded to polymeric products to boost their plasticity and enhance the workability of these materials. They are used in the production of a large number of household materials as a result of their unique features such as good insulation, great tensile strength, and outstanding corrosive resistance. They are found in indoor environments during production, storage, and usage, thereby endangering the environment. They enter the human system through inhalation, dermal contact, and food chain transmission [18].

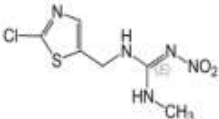
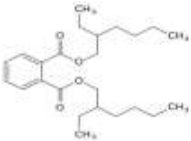
1.1.4. *Synthetic musks (SMs)* are artificial fragrance extracts that are used largely in the manufacture of personal and cosmetic materials such as skin-care lotions, and perfumes. SMs are categorized into four key classes, namely: nitro, polycyclic, macrocyclic, and alicyclic [19]. Contact with SMs products through direct skin contact, inhalation, and in-gestation can trigger serious health concerns for human physiology.

Emerging pollutants arise from our daily activities, and the list is growing as technology advances. Table 1 shows some selected emerging indoor chemical pollutants, their sources, examples, and the corresponding adverse health effects.

Table 1. Sources, compounds, and effects of emerging chemical pollutants

Emerging pollutants	Compounds	Molecular structure	Sources	Effects	References
Polybrominated diphenyl ethers (PBDEs)	Diphenyl ether, Decabromo ether		Electrical materials, building and construction items, coatings, and textiles, materials	Neurotoxicity, developmental neurotoxicity, reproductive toxicity, thyroid toxicity, immune toxicity, liver toxicity, pancreas effects, and cancer.	[17]

Phthalate esters (PAEs)	Phthalic anhydride Phthalimide Phthalhydrazide Phthaloyl chloride Benzene-1,2-dicarboxaldehyde		Plasticizers and building materials, food packaging, infant toys	congestion, irritation, and damage to lung cells.	[18]
Perfluorinated compounds (PFC)	Perfluorooctanoic Acid (PFOA), Perfluorononanoic acid		Lubricants, metal spray plating, and detergent materials	Infertility, cancer (liver bladder, and prostate)	[10]
UV-filter	Benzophenone-3, homosalate, octocrylene, 4-MBC		Air cleaners and air filters	Chest pain, coughing, shortness of breath, and wheezing.	[10]
Synthetic musk	Galaxolide (HHCB), tonalide		Cosmetics, and cleaning materials	Toxic bioaccumulation	[19,20]
Paraben	p-Hydroxybenzoic acid esters		Personal care products, indoor air dust	It causes abnormal function of the hormonal systems, which affects the male and female reproductive systems.	[21]
Polychlorinated biphenyls (PCBs)	2,3,7,8-Tetrachlorodibenzo-p-dioxin, polychlorinated naphthalene		Transformers and capacitors; oil used in motors and hydraulic systems.	Cancer, nervous, endocrine, and reproductive disorders.	[16,22]
Siloxane	Methylsiloxane		Cosmetics and skin-care products, lubricants, glues, and paints.	Malfunctioning of the reproductive system, liver difficulties, benign uterine tumors, uterine cancer, severe neurological effects, immunological effect, and a disruption of the endocrine.	[23-24]
Neonicotinoids	Clothianidin		Pollens grains, and nectar	Alteration of the normal functioning of a developing heart and brain, autism spectrum	[10]

				disorder, memory loss, and finger tremors.	
Biphenyl A	Bis(2-ethylhexyl)phthalate (BEHP)		Water bottles, food cans, storing ink, and printers.	Brain and prostate gland of fetuses, infants, and children. Abnormal behavior in children.	[24]
Transition Metals	(Vanadium, Arsenic, and Manganese)		Combustion of fossil fuels, mining, and metal smelting.	Gastrointestinal and kidney malfunctions, nervous system disorders, skin abrasions, vascular damage, birth defects, and cancer	[10]

2. Sampling and Methodology.

During the examination of these pollutants, the mode of sampling is critical for obtaining accurate and dependable results. As a result, a suitable sampling technique is required. Appropriate approach of sampling methods are chosen based on the effectiveness of either active air sampling or passive air sampling [25-26].

2.1. Active Air Sampling (AAS) Methodology

The methodology of AAS is designed such that it makes use of a pump that exerts a force that leads to the passage or flow of air samples via a trap [26]. Usually, flow meters are needed to evaluate and monitor the sample's volume or flow rate, which are characteristically measured in liters per minute. The rate of uptake is a critical factor in establishing the outcome of the concentration. This AAS method is accurate, but it can only offer incorporated concentrations within a short time [27]. Furthermore, factors such as the sorption productivity of the sorbent constituents in AAS may have an impact on overall detection accuracy [28]. Particulate phase chemicals in AAS are typically trapped on a quarter filter fibre or glass fibre filter. Vapour phase chemicals are collected on a low airflow-resistance sorbent bed, such as polyurethane foam, XAD-2 resin, Tenax, charcoal, sorbent-permeated filter, and molecularly imprinted polymers [28]. Table 2 indicates distinctive sorbents, primarily for air sampling, and their important characteristics. AAS sampling methodology is classified into three types of volume samplers: high, medium, and low [26]. High-volume samplers have been accessible for a long time due to their affordability. However, factors such as the size of the sampler, sound pollution, excessive emission of heat, large power output, and mobility make it inappropriate for indoor sampling [28]. For an appropriate sampling of the indoor environment, moderate and low-level forms of active air sampling is usually preferable. This is because both samplers require a low-flow mode of air sampling, which reduces the probability of exposure to impurities, especially when preparing the sample. The preparation of samples is a very critical part of air sampling and analysis [29].

Table 2. Types of sorbent materials and their important characteristics.

Sorbent material	Adsorption capacity	Examples	Unique characteristics	Uses
Polyurethane foam (PUF)	Resilient		low affinity for water, affordability	general
XAD (Experimental and developmental)	Resilient	XAD-2, XAD-4	high affinity for water, efficient	bulky and semi-volatile molecules.
tenax	Weak	tenax HC, tenax TA	low affinity for water, stable; low surface area; high thermal stability	volatile organic compounds with high boiling points, and are labile.
Carbon nanotubes	weak/medium	multi-walled carbon nanotubes, activated carbon, carbopack B.	low affinity for water; low permeability; friable	inert-suitable for labile components; volatile organic compounds with low boiling points.

Source: [30-31]

2.2. Passive Air Sampling (PAS) Methodology

The methodology for passive air samplers is designed in such a way that it does not require a pump. It constitutes a sorbent material with a good holding ability for the target analyte of interest [32]. PUF disks, for example, are widely used to reduce the deposits of dust and abrasive particles. Oftentimes, during sampling, the sorbent may be enclosed. The passive sampling methodology works on Fick's first law of diffusion, which is centered on free flow. The first law of Fick's on diffusion implies that complexes move from a sampled site to an assembling site through molecular diffusion [31]. PAS devices rely on diffusion that passes through a definite diffusion barricade or permeation through a membrane [32]. Because the actual uptake rate is so critical, the rate at which the mass is adsorbed as well as the duration of sampling should be precisely measured. This result is due to the samplers' design, which was created to function solely by diffusion or permeation. Furthermore, the uptake rate is comparable to the flow rate. The uptake rates of passive samplers vary depending on the sampler's design, sorbent, target analytes, sampling period, and environmental factors such as temperature, relative humidity, and air velocity [33-34]. PUF permeated with pulverized XAD resin, semipermeable membrane device, ethylene-vinyl acetate layered glass, ethylene-vinyl acetate, low-density polyethylene film, and solid-phase microextraction fibres are some of the most commonly used sorbent materials for PAS. The passive air sampling methodology is a fast, effective, and an affordable integrated method that allows an uninterrupted investigative study of minute levels of emerging pollutants (EPs) in the indoor atmosphere. The PAS methods eradicate issues concerning noisiness, cost intensiveness, and sometimes weighty and massive power requirements and general operations [35]. Furthermore, PAS examines time-weighted average concentrations of the chemicals rather than short-term concentrations [36]. Despite the numerous advantages of PAS, there are several drawbacks. Some of the drawbacks include a comparatively low sampling rate, which increases the duration of sampling, particularly for emerging pollutants at low concentrations. Furthermore, an outright quantitative determination of PAS is somewhat difficult, because it is based on the outcomes of the real measurement.

The integrity of the result is a serious criterion in the selection of a suitable method in the study of emerging indoor chemical pollutants [36]. PAS selects appropriate sorbents for the target analyte and records the duration of sampling [37]. For instance, volatile compounds may be swift to attain equilibrium, thereby making detection difficult. In addition, breakthroughs should be controlled, with a target of less than 5% in occupational sampling (38). Hence, knowledge of the suitability of diverse

sorbents for various types of emerging pollutants is required. The partitioning of the vapour phase and particulate phase also varies during sampling. To conduct a kinetic study, the uptake rate of the exact compounds must be determined, as well as the calibration of the sampler [38]. To carry out an equilibrium study, specific compound concentrations must be calculated, as well as the partition coefficient of a precise compound between the sampler and air. Furthermore, the consistency of AAS makes it ideal for short-term grab sampling. It cannot, however, signify typical concentrations or levels over a long period. As a result, PAS overcomes this disadvantage by providing the option of obtaining TWA concentrations. In conclusion, both sampling methods are suitable for collecting samples of emerging pollutants [38].

3. Instrumental Analysis of Emerging Indoor Chemical Pollutants.

Analysis of EPs from air media can be achieved by collecting air or particulate samples [9, 10]. Air samplers, dust collection, and wet and dry deposition are mediums through which particles in the air can be obtained and measured. Table 3 summarizes the various analytical techniques, sampling methods, and sorbents used for each emerging indoor pollutant.

Table 3. Selected emerging indoor chemical pollutants, sampling, and analytical techniques.

Emerging chemical pollutants	Sampling technique	Instrumental analysis	Sorbent used
Polychlorinated biphenyls (PCBs)	AAS/PAS	GC-MS	PUF
Polybrominated diphenyl ethers (PBDEs)	AAS/PAS	GC-MS	PUF
Phthalate esters (PAEs)	AAS/PAS	GC/HPLC/UHPLC	Tenax, XAD-2
Perfluorinated compounds (PFC)	AAS/PAS	LC-MS/MS	PUF
UV-filter	PAS	LC-MS/MS	PUF
Synthetic musk	AAS	GC-MS	Tenax
Paraben	AAS	HPLC	PUF/XAD-2 resin
Siloxane	AAS	GC-MS	PUF/XAD-2 resin
Neonicotinoids	PAS	HPLC	Graphitized carbon black
Bisphenol A	AAS	GC-MS/HPLC	PUF/XAD-2 resin
Benzene	PAS	GC	Carbon disulfide
Glycol	PAS	GC/MS/HPLC/MS	XAD-7
Formaldehyde	PAS	HPLC	XRD

GC-Gas chromatography; MS- Mass spectrophotometry; HPLC- High-performance liquid chromatography; UHPLC- Ultra high-performance liquid chromatography; LC- liquid chromatography; PUF- Polyurethane foam

Source: [32, 36-37]

4. Challenges encountered in the study of emerging indoor chemical pollutants and their corresponding mitigation approaches.

There are many challenges in the study of these emerging indoor chemical pollutants due to the ubiquitous and ephemeral nature of air and its constituents. More so, their physio-chemical properties and the complexity of the environmental sampling make the environmental analysis of these chemicals an extremely difficult task. Some of the challenges and mitigation approaches are shown in table 4.

Table 4. Challenges and mitigation approaches in the study of emerging indoor chemical pollutants

Challenges	Corresponding mitigation approach	References
Appropriate sampling methodology	Pre-concentration or chemical enrichment of the mode of sampling is a mitigating approach.	[39]
In-situ qualitative and quantitative determination of EPs using various detection systems	Sensor-based techniques and liquid chromatography coupled to mass spectrometry have been developed and can be used in-situ. In addition, the spectrum of analytical methods for EPs in the air needs to be broadened.	[40]

5. Conclusion and Recommendations

Emerging pollutants detected in an indoor environment have a very strong connection with mild to severe adverse health effects, such as endocrine-disrupting activities in the hormones of the body, if they are not detected quickly. The advantages and disadvantages of the two major sampling methodologies, active and passive air sampling, were discussed. Some of the challenges, as well as the mitigation strategy, were also mentioned. The study of these emerging indoor chemicals will help regulatory agencies determine the specified limit for each identified emerging indoor chemical. Furthermore, most semi-volatile organic compounds are usually partitioned between the particulate phase and the gas phase in the active air sampling methodology. As a result, both phases be adequately monitored and studied. In addition, appropriate sampling methodology, including a portable sampler capable of capturing sufficient air volume for reliable detection, as well as low-cost sampling equipment capable of collecting both vapour and particulate emerging pollutants, should be developed. More experimental and investigative research in the air media is equally needed.

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