Assessing Daily Intake of Indoor Air Pollutants from 3D Printing

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Abstract. The scientific community is increasingly focusing on indoor air quality (IAQ) more than ever, driven by ongoing research and fresh perspectives including development of 3D technologies. Exposure dose (ED_a) resulting from inhalation of indoor air pollutants emitted by 3D printers were calculated in this study. The consideration of emissions from 3D printers is based on experimental data, primarily sourced from reviewed literature. However, this research also includes some experimental values, excluding the background levels of these pollutants. Experiments were conducted using several 3D printers available (Zortrax M300 Dual) to compare the indoor air pollutants generated and their concentrations with information gathered from earlier research. In the experiments, filaments containing ABS (acrylonitrile, butadiene, and styrene copolymer material, commonly used for 3D printing) were utilized. ED_a values of styrene, toluene, formaldehyde, and acetaldehyde for 8-hour and 12hour shifts for average and maximal (reported) concentrations were calculated based on the available data. experimental and literature The average concentrations of these pollutants were determined by calculating the arithmetic mean, which incorporated concentration values obtained from previous research and experimental data collected within this study. It was concluded that further investigation should focus on aerial concentrations of styrene generated during 3D printing. Calculated ED_a for styrene from several studies exceeded the recommended guidelines for Tolerable Daily Intake (TDI) set by the World Health Organization (WHO) by at least 35%. Further exploration is imperative to incorporate additional pathways of indoor air pollutant exposure, such as skin contact and ingestion. This comprehensive approach

will provide a more thorough understanding of the overall health risks associated with indoor air quality during 3D printing.

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I. INTRODUCTION

Additive manufacturing (AM) has emerged as a transformative force in manufacturing since the late 20th century, allowing for object fabrication through layer-bylayer material addition guided by digital models. Over the past two decades, its applications have spanned diverse fields, including medicine, aerospace engineering, architecture, defence, and personal projects for consumers [1]. Advancements now focus on sophisticated materials, enabling the creation of intricate products, particularly evident in medicine where it promises breakthroughs in specialist training and therapy options. In defence, 3D printing streamlines production of lightweight, durable aircraft and vehicle components, while also facilitating rapid prototyping for weapons systems. Moreover, it supports on-demand production of spare parts in remote environments, ensuring operational readiness, and aids in crafting custom tools and unmanned aerial vehicles for reconnaissance. Overall, AM enhances agility, resilience, and technological superiority in modern military operations [1]-[6].

Despite its remarkable potential, the thermal processing involved in 3D printing raises concerns

Print ISSN 1691-5402 Online ISSN 2256-070X <u>https://doi.org/10.17770/etr2024vol3.8154</u> © 2024 Ivars Laicāns, Elīza Ķibilda, Krista Žvagiņa, Žanna Martinsone, Ilona Pavlovska. Published by Rezekne Academy of Technologies. This is an open access article under the <u>Creative Commons Attribution 4.0 International License</u>. regarding the emission of gasses, particulate matter, and volatile organic compounds (VOCs). Notably, the quantity and composition of these emissions from commercially available printers remain relatively understudied, owing to the novelty and continual innovation in the field. Research indicates that commonly used filaments in 3D printing can expose individuals to a spectrum of chemicals, potentially leading to adverse health effects like irritation of the respiratory tract, damage to the liver and central nervous system, as well as being possible carcinogens, which poses a threat to workers coming into contact with AM daily, as well as public consumers [7], [8]-[10].

A variety of different filaments are used in AM, for example, PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene) are arguably the most popular ones, providing a high level of strength, flexibility, and userfriendliness. Other filaments used that are less common are PETG (polyethylene terephthalate glycol), derived from the same polymer used to make plastic water bottles, TPE (thermoplastic elastomers), which is plastic with rubber-like qualities and many more, it being likely that other filaments may be created, suited for an array of different needs [11], [12].

Among the compounds identified in the processing of 3D printing filaments, ABS stands out as a commonly utilized material, mainly because of its simple use and print quality; price is also a beneficial factor. Studies have highlighted the occupational health risks associated with exposure to emissions from 3D printing processes. Employees working in such environments may face an increased likelihood of developing symptoms of occupational diseases, including asthma-like symptoms. When heated during printing, ABS releases emissions that contain various compounds, posing potential threats to human health, including aldehydes, acetonitrile, acetone, ethanol, formaldehyde, phenols, and toluene [1], [13]-[15].

Additionally, various factors can influence the release of VOCs during AM, such as the extrusion temperature of the filament material and the temperature of the build plate where the printing process takes place [16]. Of particular concern is styrene, a compound found in ABS filament and widely used in the production of insulation, automobile parts, and food containers. Styrene is recognized as a carcinogen, metabolizing in the human body to form styrene oxide, a toxic, mutagenic, and potentially carcinogenic compound [17]. Understanding the implications of exposure to these chemical compounds, is essential for assessing both short-term and long-term health risks associated with AM processes. Butadiene and acrylonitrile are also critical components of ABS filament used in 3D printing. Butadiene, a known carcinogen, poses health risks upon exposure, while acrylonitrile is associated with eye irritating, respiratory, and neurological effects, as well as being associated with endothelial dysfunction, which is impaired functioning of the inner lining of blood vessels, and can lead to hypertension [18]-[22]. Other compounds, such as cumene, toluene, phenol and more have been identified as emissions from AM, which can also pose a threat to the general health of workers coming into contact with these emissions. These compounds contribute to the complex mixture of emissions released during 3D printing processes [21], [23].

Quantifying the exposure dose (ED) of VOCs emitted during 3D printing is crucial for assessing indoor air quality and safeguarding human health as well as for calculating the resulting estimated daily intake (EDI). EDI refers to the quantity of a substance that an individual can consume each day throughout their lifetime without posing a health risk. Typically, it is stated as milligrams of the substance per kilogram of body weight per day [24]. Measurements of aerial concentrations of such pollutants helps identify potential health risks associated with prolonged exposure to indoor environments where 3D printing occurs. By measuring the intake of VOCs, researchers can develop strategies to mitigate exposure and to identify the need for enhancing ventilation systems in spaces where 3D printing takes place. Moreover, quantifying ED or/and EDI provides valuable data for regulatory agencies to establish guidelines and standards aimed at protecting individuals from harmful airborne pollutants generated by 3D printers. Ultimately, a comprehensive assessment of EDI facilitates informed decision-making and promotes safer practices within the rapidly expanding domain of AM. Tolerable daily intake (TDI) is an estimate of the amount of a specific substance in air inhaled daily over a lifetime without appreciable health risk and used to compare the calculated EDIs and identify the potential chemicals that pose health risks [1], [21], [25], [26].

The objectives of this study include identifying the most hazardous chemicals emitted during 3D printing by analysing available experimental data from literature reviews and on-site experiments. Additionally, the study aims were to calculate the ED for styrene, toluene, formaldehyde, and acetaldehyde, and theoretically compare these values with the TDI to assess the potential health risks associated with 3D printing emissions.

II. MATERIALS AND METHODS

The ED, EDI and TDI are crucial parameters in assessing the potential health effects of exposure to various substances. In this study, all these parameters were investigated for 3D printing related substances, focusing on their significance in risk assessment and regulatory decision-making. The ED calculation was employed and subsequently compared to the corresponding TDI, which was chosen based on previous research findings.

The experimental setup featured a printing area, which comprised a room with a volume of 52.5 m^3 . Within this area, two 3D printers (both "Zortrax M 300 Dual") were positioned at a height of 70 cm, with a distance of 1 m between them. Throughout the experiment, both printers utilized "Ultrat" filament in black colour. The build plate temperature was maintained at $+105^{\circ}$ C, while the nozzle temperature was set to $+260^{\circ}$ C. Air samples were collected using two individual samplers (Gillian LFS -113DC), placed equidistantly between printers. The samples were simultaneously collected on the solid sorbent cartridges treated with 2,4-dinitrophenylhydrazine (DNPH cartridges for low molecular aldehydes). Subsequently, all samples were analysed using a Highperformance liquid chromatograph (HPLC) – "Water Alliance 2695" with a UV detector – "Water 2487".

The experiments were conducted separately three times, both for blank samples and for the experimental samples. The blank samples were collected in the same room 120 minutes before the experimental samples. Prior to collecting the blank samples, it was ensured that there had been no printing activity in the room for at least 10 hours and the room would be properly ventilated. Both the blank and experimental samples were collected for 60 minutes at a flow rate of 0.1 L/min. Following the sample recording process, they were stored in a container with refrigerants and then transported to the laboratory for analysis. The experimental samples were initiated 45 minutes after the 3D printers started, allowing time for the printers to reach their operating temperatures. The air samplers were positioned on the table between the 3D printers. Both printers were equipped with "HEPA" filters and enclosed casings, which were fully closed and operational during the air sampling process. The results were analysed, and the blank samples were utilized to adjust for the baseline levels of acetaldehyde and formaldehyde that were not attributed to the 3D printing.

The EDI is one of the parameters to assess the potential health effects. The formula for EDI encompasses the summation of ED from various exposure routes including inhalation, ingestion via water, ingestion via soil, ingestion via food, dermal contact with water, and dermal contact with soil (Equation 1) [27].

$$EDI = ED_a + ED_w + ED_s + ED_f + ED_{ws} + ED_{ss}$$
(1)

- EDI estimated daily intake;
- ED_a the amount inhaled through the air;
- ED_w the amount taken by drinking water;
- ED_s the amount taken by ingesting soil;
- ED_{f} the amount taken in by food;
- ED_{ws} the amount absorbed through skin contact with water;
- ED_{ss} the amount absorbed through skin contact with the soil.

In specific circumstances, EDI aligns with ED_a , mainly due to airborne inhalation serving as the primary route of exposure in 3D printing scenarios, with other pathways being non-specific in this context. As a result, for further calculation the following equation (Equation 2) were used [27]:

$$ED_a = \frac{C*IR*EF*X}{24*BW} \tag{2}$$

- ED_a exposure dose, mg/kg/day, exposition to a chemical substance;
- C concentration of a chemical in air, mg/m^3 ;
- IR inhalation rate inhaled amount of air in a day, 23 m³/day;
- EF exposure factor, unitless (how often the person is exposed to a chemical);
- X hours in a day exposed to a chemical;
- hours in a day;
- BW body mass, kg (it was assumed that the average value for adult body mass is 70 kg) [28].

The average and maximal concentrations of chemical substances used in the calculation of ED_a were predominantly obtained from previously collected data from various scientific publications (see Table 1). The selection of aerial concentration values from previous studies was carefully performed, prioritizing reliability and precision.

The calculated ED_a specifically pertains to the amount of the particular chemical inhaled and encompasses both the highest and average airborne concentrations recorded for each chemical.

| TABLE 1 AIRBORNE CHEMICAL COMPOUND |
|--|
| CONCENTRATIONS CONSIDERED FOR CALCULATIONS |

| | Concentration, µg/m ³ | | | | |
|----------------------|---|------------|---------|--|--|
| Chemical compound | Literature data [source] | Maximal | Average | | |
| Styrene | 912.8 [16]; 461.0 [16]; 243.2 [16]; 857.7 [16]; 12.0 [28]; 101.0 [29]; 252.1 [30]; 212.1 [30]; 100.5 [30] | 912.8 [16] | 338.9 | | |
| Toluene | 31.5 [16]; 37.8 [16]; 40.4 [16]; 49.0 [28]; | 49.0 [29] | 39.7 | | |
| Formaldehyde | 37.0 [28]; 16.0 (measured) | 37.0 [29] | 26.5 | | |
| Acetaldehyde | 15.0 [28]; 16.3 [30]; 7.7 [30]; 11.1 [30]; 13.7 [30]; 2.6 (measured) | 16.3 [30] | 10.0 | | |

Regarding to the relevant exposure factor (EF) necessary for calculation of the ED_a , the following equation (Equation 3) with the values specified below was used:

$$EF = \frac{30*48*5}{70*365} = 0.28 \text{ (unitless)} \tag{3}$$

EF - exposure factor;

30 - assumed number of years worked at the job where the source of chemical occurs;
48 - work weeks in a year, assuming there is 4 weeks' vacation time every year;

5 - workdays in a week;

70 - assumed lifetime (standard value in toxicological studies [27]);

365 - number of days in a year.

The consistent EF value of 0.28 in all calculations, was utilized to reach ED_a and ED values (see Table 2 and Table 3).

III. RESULTS AND DISCUSSION

In this experiment, following aerial concentration values during 3D printing were obtained for formaldehyde (16.0 \pm 2.0 $\mu g/m^3$) and acetaldehyde (2.6 \pm 0.3 $\mu g/m^3$). These values were included in overall calculation of the average concentrations of aerial chemical concentrations (Table 1).

These values differ significantly from the values published by previous researchers [28], [31]. Specifically, the aerial concentration of formaldehyde recorded during 3D printing with ABS-containing filament is 56% lower than values in prior published report (only one study was identified with a single value [32]), while the acetaldehyde concentration is 80% lower than the average of previously reported findings.

Despite the fact that both obtained values were significantly lower than the previously reported for these specific chemicals (formaldehyde and acetaldehyde) they were included in the calculation of the average aerial concentrations, which later were used to calculate the ED_a. This decision was based on factors that each of the experiment viewed had slightly different setup, but the main reason was that the authors found through the literature analysis that small individual chemical composition variances, like different colour of the same brand filament, may largely affect the quantities of individual VOCs. Therefore, significant deviancies of the individual VOC concentrations between different ABS filaments don't necessarily represent faulty values.

Calculated ED_a were compared against established guidelines for TDI, serving as a critical benchmark to evaluate the potential risks posed by exposure to indoor air pollutants (Table 2). This comparative analysis facilitated a deeper understanding of the potential health impacts associated with 3D printing emissions.

The findings of this study suggest that calculated styrene exposure, whether based on maximal aerial concentrations or average concentrations, pose the greatest health risks when compared to their TDI value. The calculated ED_a values were directly compared with TDI values, revealing that the ED_a for styrene average concentration exceeds the TDI by 35%. This indicates that emissions of styrene from 3D printers could potentially lead to health issues for personnel working with these devices in long-term. The real intake of styrene for individuals working with 3D printers using ABS filament materials would likely be higher. However, it was not feasible to compute the complete intake.

TABLE 2 ED_a RESULTS OF AIRBORNE CHEMICAL COMPOUNDS BASED ON AVERAGE AND MAXIMAL CONCENTRATIONS AND CORRELATION WITH TDI VALUES

| Chemical compound | | Caerial, µg∕m ³ | ED _a , μg/kg <i>(8 h)</i> | ED _a , μg/kg (12 h) | TDI, μg/kg |
|-------------------|-----|-------------------------------|--|--------------------------------------|---------------|
| Styrene | max | 912.8 | 28.0 | 42.0 | 7.7 [31] |
| | avg | 338.9 | 10.4 | 15.6 | 7.7 [31] |
| Toluene | max | 49.0 | 1.5 | 2.3 | 1070 [30] |
| | avg | 39.7 | 1.2 | 1.8 | 1070 [30] |
| Formaldehyde | max | 37.0 | 1.1 | 1.7 | 150 [32] |
| | avg | 26.5 | 0.8 | 1.2 | 150 [32] |
| Acetaldehyde | max | 16.3 | 0.5 | 0.7 | 100 [33] |
| | avg | 10.0 | 0.3 | 0.5 | 100 [33] |

This research opted to exclude the background levels of observed chemical components, although it was deliberated that such exclusion might not be necessary as background levels contribute to the chemicals absorbed through the lungs. Moreover, there was a hypothesis suggesting that in areas continuously used for 3D printing, various chemical air contaminants could potentially accumulate, resulting in elevated background levels of relevant chemicals.

While the data sources for aerial levels of chemical compounds were assessed and evaluated, it is noteworthy that variations in experimental design across the studies introduce a certain degree of uncertainty.

According to the Fig. 1 and Table 3, the concentrations of four distinct chemical compounds (styrene, toluene, formaldehyde, and acetaldehyde) across time intervals ranging from 1 hour to 24 hours, including 8-hour shift and 12-hour shift were presented.

TABLE 3 EXPOSURE DOSE OF CHEMICAL COMPOUNDS

| Chemical | С, | Exposure dose, µg/kg/day | | | | |
|--------------|-------------------------------|--------------------------|-----|------|------|------|
| compound | μg/m ³ (aerial) | 1 h | 4 h | 8 h | 12 h | 24 h |
| Styrene | 338.9 | 1.3 | 5.2 | 10.4 | 15.6 | 31.2 |
| Toluene | 39.7 | 0.2 | 0.6 | 1.2 | 1.8 | 3.7 |
| Formaldehyde | 26.5 | 0.1 | 0.4 | 0.8 | 1.2 | 2.4 |
| Acetaldehyde | 10.0 | 0.04 | 0.2 | 0.3 | 0.5 | 0.9 |

The concentration of chemical compounds increases gradually over time. This indicates a significant increase in concentration over the observed time period.

Exposure to styrene, toluene, formaldehyde, and acetaldehyde in 3D printing occurs primarily through inhalation of emitted vapor and particles during the printing process. Short-term exposure can result in irritation of the respiratory tract and eyes, dizziness, and headaches. Long-term exposure to these chemicals has been linked to respiratory issues, neurological effects, and potential carcinogenicity, highlighting the importance of proper ventilation and personal protective equipment to mitigate health risks associated with 3D printing. These calculations provide valuable insights for employees and employers as well as regulatory and risk management purposes.

For instance, the average concentration of styrene rises from approximately 1.3 mg/kg/day at 1 hour to 31.2 μ g/kg/day at 24 hours indicating a notable increase.

Similarly, toluene, formaldehyde and acetaldehyde also demonstrate substantial increases in concentration from their initial levels from 0.2, 0.1, 0.04 to 3.7, 2.4 and 0.9 μ g/kg/day, respectively, after 24 hours, highlighting the dynamic nature of airborne pollutant levels over time.

Analysing ED_a can also guide efforts to optimize 3D printing processes to reduce emissions of hazardous chemicals. This may involve modifying printing parameters, using alternative materials, or implementing post-processing treatments to mitigate emissions. ED_a data serves as valuable input for research and development efforts aimed at improving the safety of 3D printing technologies. Researchers may use this information to develop safer materials, printing methods, and workplace practices.



Fig.1. ED_a for styrene, toluene, formaldehyde, and acetaldehyde for working hours: 1 h, 4 h, 8 h, 12 h, and 24 h.

IV. CONCLUSIONS

This study highlights the necessity of thorough attention to concentrations of chemical compounds during 3D printing processes. The reported levels, as well as obtained experimental data for aerial concentrations of styrene, toluene, formaldehyde, and acetaldehyde during 3D printing, were utilized to compute the ED_a, which was subsequently compared to established thresholds for chemical intake, namely TDI. The outcomes of these computations suggest that individuals involved in 3D printing tasks (utilizing ABS filaments) may face a potential health hazards of chemical exposure, especially of styrene. More specifically, the ED_a calculated for styrene within 8-hour shift exceeds the TDI by 35% for average concentrations and by more than threefold for maximal styrene concentration observed during 3D printing. The other chemical compounds such as toluene, formaldehyde and acetaldehyde which are produced in 3D printing while using ABS copolymer as a filament material are highly unlikely to pose potential health risks from daily inhalation. The significant inequality between

the calculated ED_a for styrene and the established TDI thresholds underscores the heightened risk of adverse health effects, including respiratory and neurological issues, for individuals exposed to these concentrations during their working hours.

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