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EFFECTIVE AIR MONITORING BASED ON PASSIVE AIR SAMPLING WITH POLYURETHANE FOAM DISKS FOR PERSISTENT ORGANIC POLLUTANTS

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Abstract: The Stockholm Convention, established by the United Nations Environment Programme (UNEP), aims to protect human health and the atmosphere against Persistent Organic Pollutants (POPs) in the air, water, and soil. The Stockholm Convention's conference of parties selected air as a core matrix because it is an important medium for tracking the long-term movement of POPs. The Stockholm Convention's global monitoring plan (GMP) utilizes the passive air sampling to reduce the POPs in the air environment. Passive air sampling plays essential role in the environmental monitoring which provides time-integrated data on the presence of pollutants in the environment. It relies on the natural process as the movement of molecules called diffusion to transfer contaminants from the environment (air, water, or soil) to a collecting medium. The sampler design enables the controlled passage of gases and particles onto a collecting medium, such as a sorbent. Many underdeveloped countries face special obstacles in monitoring air quality, notably POPs such as dioxins. From this, the passive air sampling with sorbents to be a valuable forms addressing the resource constraints, accessibility limitations, and improving the data collection, public health measures.

This study conducts a research work on passive air sampling technique using Polyurethane foam (PUF) disk as sorbent material in the passive air sampler aimed at investigating the atmospheric concentrations and sources of POPs in four cities including Kanyakumari, Noida, Mysore, and Pune of India along five sectors such as electronic waste, information technology, industrial, residential, and dumpsites. For the purpose of determining interurban emission sources, this research work utilizes Trajectory Modelling, Positive Matrix Factorization and Principal Component Analysis for data analysis. The Trajectory Modelling identifies the movement of air masses, Positive Matrix Factorization discovers the dominant emission sources for specific pollutants and Principal Component Analysis obtains dimensionality reduction with the extraction of influential components in the data.

Index Terms **- Passive Air Sampling, Passive Sampler, Polyurethane Foam Disk, Persistent Organic Pollutants, Air Monitoring.**

I. INTRODUCTION

Air quality is a significant issue in both developed and developing nations. Air pollution is a severe environmental issue that impacts both the environment and human health. Recently, there has been an upsurge in interest and demand for both indoor and outdoor air analysis. A wide range of POPs is present in ambient air. POPs pose a significant threat due to their long-lasting nature, high toxicity, and bioaccumulation.

Air sampling is conducted in two ways such as active or passive sampling. The active sampling necessitates a complicated and costly sampler with a calibrated pump. The passive air sampling is a cost-effective and easy-to-deploy to obtain time-integrated data on airborne contaminants. The passive air sampling is a powerful method of environmental monitoring for accumulating the chemical contaminants (POPs) in the environment over time with the aid of collecting medium including man-made device or a biological organism. The function of passive air samplers is to serve as silent sponges for absorbing the contaminants over a defined period of time. Scientists evaluate the long-term trends and average pollutants concentrations to obtain a comprehensive understanding of types and qualities of pollutants present in the air over the sampling period.

In [1], the study was carried out for performing air monitoring by utilizing the passive samplers with PUFs while determining the Dioxin-Like POPs in Developing Countries (2017-2019). It falls under the Stockholm Convention's Global Monitoring Plan for POPs. However, the temperature and humidity were affected the efficacy of PUF samplers in capturing dl-POPs from the air, thereby leading to discrepancies in reported concentrations.

In [2], the passive air sampling was deployed for assessing the Polychlorinated Dibenzo-p-Dioxins/Furans (PCDD/Fs), Polychlorinated Biphenyls (PCBs), Phthalate Esters (PAEs), Di-ethylhexyl adipate (DEHA), and Polycyclic Aromatic

Hydrocarbons (PAHs) from informal electronic waste recycling and allied sectors in Indian megacities. But, it did not effectively capture the pollutants within each group (PCDD/Fs, PCBs, PAHs, etc.) regarding the sampler type.

In [3], the study was carried out for performing the passive air sampling with the objective of monitoring the Perfluoroalkane Substances (PFAS) in developing countries between 2017 and 2019. In [4], the passive air samplers were employed for estimating the Volatile Organic Compounds (VOCs) during the FIREX-AQ campaign, depending on the determination of diffusive uptake rates (DURs). However, it was difficult to distinguish between VOCs that are extremely similar.

In [5], the POPs and chemicals of emerging concern (CECs) in urban air across the globe were analyzed in a significant manner. In densely populated urban areas, distinguishing between POPs and CECs was challenging. In [6], the variability in measurements of semi-volatile organic compounds (SVOCs) was investigated through the utilization of Polyurethane Foam (PUF) passive air samplers. However, it did not taken into account the influence of long-term deployment (months or years) on sampler performance and potential degradation.

In [7], the feasibility of using **passive air samplers** combined with **non-targeted analysis** techniques were investigated for discovering the **POP-like chemicals** in the atmosphere. In [8], the passive air samplers were deployed for examining the presence of POPs in the atmosphere of three Chilean cities: Santiago (STG), Concepción (CON) and Temuco (TEM).

The chemicals released from tire wear in megacities around the world were examined in [9] while implementing the passive air samples. In [10], the comparative passive air sampling method was introduced for estimating the presence and distribution of POPs in the atmosphere across various countries worldwide. In [11], the High spatial resolution measurements of passive-sampler were determined for evaluating the air concentrations of POPs in the Campania region, Italy. But, the POPs were difficult to trace back to specific sources in a complicated region due to air transport and pollutant mixing.

In [12], the Assessment of seasonal variations in POPs across the region of Tuscany using passive air samplers were determined by deploying the Passive air samplers with the polyurethane foam (PUF) disks over four sampling periods of 3 and 5 months from April 2008 to July 2009 in urban and rural sites. In [13], the POP's temporal trends in Africa over a decade were investigated through the utilization of MONET passive air sampling. However, it failed to discover the long-range transport of pollutants from outside Africa.

In [14], the regional monitoring was carried out for determining the POPs and emerging compounds in Kolkata and the Sundarban, a rural mangrove wetland in India by utilizing the passive air samplers. In [15], the research work explored the use of pine tree components, specifically needles and branches as passive air samplers for monitoring the POPs including Polycyclic Aromatic Hydrocarbons (PAHs), Organochlorine Pesticides (OCPs), and Polychlorinated Biphenyls (PCBs). However, the factors like tree species, age, and environmental conditions which all had an impact on POP's uptake by trees, putting uncertainty into predicted air POP's concentrations.

Contributory remarks

The following list summarizes the contributions made by this research work.

- The research work provides a cost-effective way to collect air samples over a set period by employing the passive air samplers with PUF disks across Indian cities.
- The research utilizes the potent mix of approaches to detect pollution sources from informal electronic trash recycling and related businesses in Indian cities.
- In the research work, the **Trajectory Modelling** is implemented for discovering the backward trajectories of air masses arriving at the sampling locations.
- The **Positive Matrix Factorization** is designed in the research work in order to differentiate the contributions of the pollutants from various emission sources based on the unique chemical fingerprints of pollutants associated with each source.
- The **Principal Component Analysis** is carried out in the research work to identify the underlying patterns in the pollutant data and potentially group sampling locations with similar pollutant profiles
- Finally, the results and discussions are carried out to estimate the performance of this research work.

Organization of the paper

An outline of this paper is provided below. In the Section 2, the study region and observational data are introduced. Besides, the related works are examined in Section 2. Section 3 introduces details of our research work for air monitoring by determining the POPs using passive air samplers with PUF disks. The experiment's findings and analysis are reported in the Section 4 and 5. Section 6 concludes with some final thoughts.

II. RELATED WORK

In [16], the PUF-based passive air samplers were designed for the purpose of determining the Polycyclic Aromatic Hydrocarbons (PAHs) and POPs in the informal waste processing and urban areas, northern Vietnam. However, it was not able to effectively differentiate the highly similar molecules. In [17], the ceramic adsorbent was utilized as a passive air sampler with the goal of monitoring three pollutant groups such as Organochlorine Pesticides (OCPs), Polycyclic Aromatic Hydrocarbons (PAHs), and Polychlorinated Biphenyls (PCBs) in outdoor air.

In [18], the semi volatile organic contaminants (SVOCs) in indoor air were determined by calibrating silicone samplers. But, the indoor areas contain a wide range of SVOC mixes, as well as variables such as ventilation and temperature, which can influence uptake when compared to laboratory conditions. In [19], the importance of calibrating passive air samplers made of PUF was examined for achieving the accurate measurement of airborne pollutants.

In [20], the MONET Passive Air Sampling was implemented for examining the long-term concentrations of 20 POPs monitored at 32 sites in 27 European countries. But, environmental factors such as temperature and humidity can have an impact on the efficacy of passive samplers in catching contaminants, potentially leading to uncertainty in reported concentrations.

In [21], the research work was implemented for performing the spatial distribution and source identification depending on the passive air sampling regarding specific group of air pollutants - halogenated polycyclic aromatic hydrocarbons (Halo-PAHs) - in

the largest industrial city of Korea. However, the selected places were not reflecting the entire city, limiting the generalisability of the results.

In [22], the study was carried out for observing the High quantities of VOCs were detected in the center and southwest of Seoul using passive air samplers installed at 36 sites in Seoul, Korea, during the summer and winter. However, the source attribution was complicated by factors such as air movement and the mixing of pollutants from numerous sources within a populous metropolis like Seoul.

In [23], the tree bark was utilized as a passive air sampler in order to investigate the concentrations, sources, and distributions of polycyclic aromatic hydrocarbons (PAHs), Organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs), along with their cancer risks across Nepal. But, it failed to account for individual variability in health risk assessment due to the varying susceptibility to pollutants based on age, genetics, and overall health.

In [24], the passive air samplers were implemented with the objective of obtaining the spatial distribution, seasonal variations, and source identification by examining the polycyclic aromatic hydrocarbons (PAHs) in Seoul, South Korea. But, it was not able to obtain the information about the precise features of the captured PAHs (for example, the number of rings).

In [25], the spread and presence of POPs and current-use pesticides (CUPs) in the atmosphere of Argentinean Patagonia were investigated. Through this study, the spatial distribution (variation across different locations) and temporal distribution (changes over time) of POPs and CUPs were examined successfully. But, the variations in pollution levels across wide and diverse environments may not be completely captured. The miniaturized active air sampling technique was implemented in [26] with the aim of examining the tire rubber pollutants in indoor and outdoor air.

In [27], the study was examined the time trends of the organic contaminants in air from eight arctic sties over a 25 year period. However, it failed to effectively pinpoint the exact sources of the pollutants. In [28], the research work was designed to comprehend the impact of temperature on the capacity of PUF samplers to extract volatile organic compounds from the air. However, the extensive calibration and data analysis were necessary to comprehend temperature influence for certain VOC.

In [29], the research work was carried out for performing the two year global monitoring of POPs including polychlorinated biphenyls (PCBs), Organochlorine pesticides (OCPs), polybrominated diphenylethers (PBDEs), one polybrominated biphenyl and hexabromocyclododecane (HBCD) diastereomers in the air from 43 countries of Asia, Africa, Latin America, and the Pacific while utilizing the PUF disks in the passive samplers.

In [30], the usage of passive samplers was investigated with the purpose of monitoring the Volatile Organic Compounds (VOCs) in the air surrounding petrochemical facilities in Tarragona, Spain, between 2019 and 2021. This study examined the environmental implications of petrochemical companies and recommended the implementation of policies to limit VOC emissions. However, industrial activities may result in short-term surges in VOC emissions that cannot be collected. The inadequacy of traditional work to accurately assess POPs in the air, as previously stated, motivated this investigation. These strategies are detailed in more detail in the section that follows.

III. PROPOSED METHODOLOGY

In developing countries, the informal electronic waste recycling sector is causing toxic chemical emissions. The issue of electronic waste recycling has become a pressing concern due to the lack of accurate data on emissions from misreported waste inflows. The electronic waste recycling poses significant environmental and human health risks due to hazardous recycling procedures. India has documented significant emissions of POPs as PCDD/Fs (Polychlorinated dibenzo-p-dioxins and furans), PCBs (Polychlorinated biphenyls), **Plasticizers and PAHs (Polycyclic Aromatic Hydrocarbons)** from crude dismantling, open burning of electronic coatings, and other chemical processes in the electronic waste.

The dioxin is a group of chemical compounds called **polychlorinated dibenzo-p-dioxins (PCDDs)** which are exceedingly harmful compounds and remain in the environment for decades or even centuries. The dioxins are extremely poisonous and can cause serious health consequences. For that reason, the process of monitoring dioxins is vital for public health, environmental protection, and policy decision-making to reduce the human and ecological exposure to dangerous chemicals. The potential exposure hazards are discovered before they cause harm by monitoring dioxin levels in the environment.

Passive sampling methods help in monitoring the presence of contaminants in the environment over time. The passive samplers are mainly classified into two different kinds of passive samplers such as sorbent-based samplers and bio-monitoring samplers. The sorbent-based samplers utilize materials like resin or membranes to absorb environmental contaminants. The bio-monitoring samplers utilize living organisms such as mussels or tree leaves for accumulating the contaminants from the environment.

During passive air sampling, the sampler design allows for **controlled diffusion** of gases and particles onto a collecting medium, such as a sorbent material. The passive air sampling is the process of capturing the airborne contaminants in the air to effectively monitor air quality and assess potential risks associated with airborne pollutants. The widely utilized methods for passive air sapling are diffusion, sorption and permeation according to the consideration of essential aspects such as target pollutants, sampling duration, detection limits and environmental conditions. In the passive air samplers, the air pollutant is collected onto sorbent media like polyurethane foam (PUFs) or XAD-2 resin through natural air diffusion over a set period.

The passive air sampling analytics entail a number of steps for converting acquired samples into useful environmental data. Different kinds of analytical techniques like gas chromatography or mass spectrometry can be used to analyse pollutants based on the target pollutants and the sorbent used. Scientists can determine the types and quantities of contaminants in the air throughout a certain sampling period by evaluating the obtained data. The analyzed information helps in environmental monitoring, exposure assessments and regulation deployment.

In our research work, the sorbent-based passive air sampler is used for monitoring the POP as dioxin. The sorbents are unique materials utilized in air monitoring to absorb and concentrate the airborne contaminants. Sorbents, with their high surface area and specific affinity for pollutants act as sponges which attract and hold them from the surrounding air. The air monitoring uses a wide range of sorbents, including Polyurethane Foam (PUF), Activated Carbon, XAD-2 Resin, and Silica Gel. The Stockholm Convention is an international pact that attempts to eradicate or prohibit the production and use of several POPs including dioxins by utilizing the passive air samplers with PUFs. The framework of Stockholm Convention's global monitoring plan establishes a

consistent approach for determining POP concentrations, providing accurate information on their long-term presence in the environment, trends over time, and regional and worldwide movement.

The main motivation of this research work is to assess the several classes of pollutants such as PCDD/Fs (Polychlorinated dibenzo-p-dioxins and furans), PCBs (Polychlorinated biphenyls), **Plasticizers,** and **PAHs (Polycyclic Aromatic Hydrocarbons).** Here**,** PCDD/Fs are Highly toxic compounds**,** PCBs Including dioxin-like PCBs (dl-PCBs), Including dioxin-like PCBs (dl-PCBs) like **DnBP (Di-n-butyl phthalate)** and **DEHP (Di(2-ethylhexyl) phthalate),** and **PAHs** are commonly found in combustion process.

There are several steps to be carried out for performing passive air sampling analytics by converting the collected samples into meaningful environmental data. As the first step, the sample deployment which includes selection of site, preparation of sampler, and setting of sampling duration is carried out. According to the monitoring objectives such as industrial areas, the appropriate locations are selected. The sample preparation process involves calibrating and deploying selected passive air samplers in accordance with established protocols. The sampling period is set for capturing relevant data (hours, days, weeks) while taking into account the target pollutants. After this, the sample retrieval and storage are performed as a second step. The samplers from deployment locations are retrieved and relevant information like sampling location, duration, and any environmental observations are recorded. Then, the samples under appropriate conditions (temperature, light) are stored for reducing the degradation of captured pollutants. Followed by, the sample analysis is carried out with the performance of three processes such as extraction, cleaning, and instrumental analysis. The captured pollutants from the sorbent material are extracted as the performance of sample extraction by utilizing appropriate solvents. Then, the cleaning and analysis processes are carried out for identifying and quantifying the target pollutants. Figure 1 illustrates the overall process passive air sampling with PUF for air monitoring.

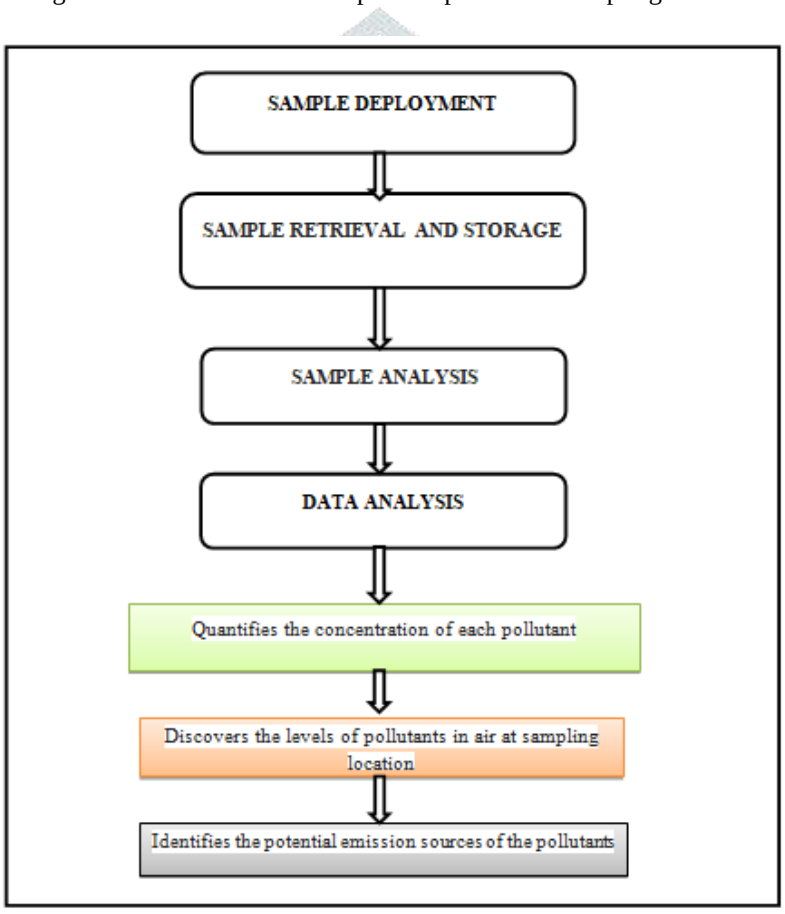

Figure 1 Overall flow process of passive air sampling with PUF for air monitoring

At first, the sample deployment stage includes site selection, sample preparation, sampling duration is carried out by deploying the passive air samplers utilizing PUF disk in each of four cities such as Kanyakumari, Noida, Mysore, and Pune for investigating the air pollutants from the five different sectors as follows. Electronic waste - Associated with informal electronic waste recycling, Information Technology - Relevant to the IT industry, Industrial-Reflecting industrial activities, Residential-Representing residential areas, and Dumpsites- Associated with waste disposal sites. The representative locations across five different sectors in four cities are selected. The passive air samplers using PUF disks are prepared. The passive air samplers with PUF disks are deployed at selected locations for a specific sampling duration. Secondly, the PUF disks from the deployment sites are retrieved after the sampling period. Here, the gathered PUF disks in appropriate containers are stored at low temperatures (around -20°C) for preventing the contaminant degradation. Followed by, the sample analysis is performed in order to detect and quantify the target pollutants. Here, the sample analysis involves three essential steps such as sample extraction, cleanup, and instrumental analysis. The pollutants (PCDD/Fs, PCBs, PAEs, DEHA, and PAHs) from the PUF disks are extracted by utilizing hexane and they are cleaned up with the help of multi-layer chromatography columns. By this, different pollutant groups are separated. The cleaned extracts are examined by utilizing the high-resolution Gas Chromatography coupled with High-Resolution Mass Spectrometry (HRGC/HRMS). Finally, the data analysis which includes quantification, evaluation, and identification is performed. According to the instrumental response compared to calibration standards, the concentration of each pollutant is quantified. The data is determined for understanding the levels of PCDD/Fs, PCBs, PAEs, DEHA, and PAHs present in the air at each sampling location. Then, the Trajectory Modelling, Positive Matrix Factorization, and Principal Component Analysis are

carried out for discovering the potential emission sources of the pollutants. Therefore, the effective detection of presence and potential sources of these pollutants in the air helps in performing task involves analyzing and interpreting data related to air quality and potential health risks.

In this research work, the passive air sampling with PUF disks are implemented in four cities (Kanyakumari, Noida, Mysore, and Pune) of India for obtaining the goal of investigating the existence of atmospheric and POPs (PCDD/Fs, PCBs, Plasticizers **(**PAEs and DEHA**),** and PAHs) along five unique sectors (electronic waste, information technology, industrial, residential, and dumpsites). The four major procedures involved in the examination of target pollutants are sample deployment, sample retrieval and storage, sample analysis, and data analysis which are discussed in detail below.

SAMPLE DEPLOYMENT:

In order to carry out the air monitoring, the passive air sampling plays an essential role for determining the target contaminants in the air environment. Each passive air sampler consists of an upper and lower bowl (upper bowl is bigger than lower bowl), one thread axis, two distance tubes (one short with 7cm and one large with 10cm), four flat washers, two nuts, one wing nut, one hanging hook, and one hook adaptor. Figure 2 depicts the passive air sampler.

Figure 2 Passive air sampler devices

In this research work, the passive air sampling is carried out by employing the specialized passive air samplers containing sorbent material like PUF disks at certain locations for collecting the pollutants over a set time period (days or weeks) without needing external power. Figure 3 shows the schematic diagram of passive air sampler with PUF disk.

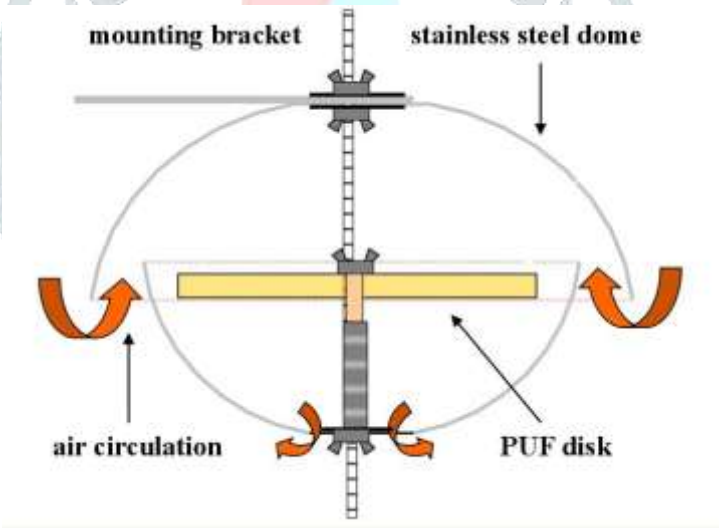

Figure 3 Schematic diagram of passive air sampler with PUF disk

At the initial step, let consider '$n = 25$' number of passive air samplers using PUFs which were deployed in four major sampling cites of India including Kanyakumari, Noida, Pune, and Mysore along five sectors such as electronic waste, information technology, industrial, residential, and dumpsites. [Kanyakumari ('$n = 10$'), Noida ('$n = 8$'), Pune ('$n = 2$') and Mysore ('$n = 5$')]. The electronic waste sector is associated with known or suspected informal electronic waste recycling areas within the cities. The information technology sector is relevant with the areas which have high concentration of information technology companies and offices. The industrial sector represents the industrial areas that might contribute to the target pollutants. The residential sector covers the typical residential zones within the city. The dumpsites sector is related with active or recently closed waste disposal areas. 25 number of passive air samplers with PUFs were deployed for 28 days between January and February 2015 within the cities. This research work is utilized a sampling rate of 3.5m3/day for consistency in obtaining the time integrated concentration of POPs, PAHs, and plasticizers from previous studies. Each passive air samplers are identified by its location, sampler identification code, start and end dates as shown in below table 1.

Table 1 Identity of passive air samplers

Cities	Location (Sector)	Sampler Identification Code	Starting And Ending Dates Of Sampling (28 days)
Kanyakumari	Electronic waste	Ew1	02-01-2015 to 29-01-2015
	Electronic waste	Ew2	02-01-2015 to 29-01-2015
	Information technology	It1	02-01-2015 to 30-01-2015
	Information technology	It2	02-01-2015 to 29-01-2015
	Residential	Re5	02-01-2015 to 29-01-2015
	Industrial	In1	03-01-2015 to 30-01-2015
	Industrial	In2	02-01-2015 to 29-01-2015
	Industrial	In3	02-01-2015 to 29-01-2015
	Dumpsite	Du1	03-01-2015 to 30-01-2015
	Dumpsite	Du2	05-01-2015 to 01-02-2015
Noida	Electronic waste	Ew3	05-01-2015 to 01-02-2015
	Electronic waste	Ew4	05-01-2015 to 01-02-2015
	Electronic waste	Ew5	05-01-2015 to 01-02-2015
	Information technology	It3	07-01-2015 to 03-02-2015
	Residential	Re1	07-01-2015 to 03-02-2015
	Industrial	In4	07-01-2015 to 03-02-2015
	Industrial	In5	07-01-2015 to 03-02-2015
	Dumpsite	Du3	05-01-2015 to 01-02-2015
Pune	Residential	Re2	02-01-2015 to 29-01-2015
	Residential	Re3	02-01-2015 to 29-01-2015
Mysore	Electronic waste	Ew6	03-01-2015 to 30-01-2015
	Electronic waste	Ew7	05-01-2015 to 01-02-2015
	Information technology	It4	05-01-2015 to 01-02-2015
	Residential	Re4	05-01-2015 to 01-02-2015

SAMPLE RETRIEVAL AND STORAGE:

After the predetermined sampling deployment period, the samplers from each location are retrieved. The samplers need to store in a cool, dark environment to prevent potential loss of pollutants until further processing. The PUF disks are maintained in freezers at -18°C until analysis or sent to a reference lab.

SAMPLE ANALYSIS:

In this stage, the sample extraction, chemical separation, and instrumental analysis are involved. In the lab, the PUF disks were carefully removed from the sampling devices and the adsorbed pollutants are extracted from the PUF disks using appropriate solvents (such as hexane or dichloromethane). The PUF disks were extracted with 150mL of toluene in the Soxhlet device for 24 hours with an average of six cycles per hour.

The extracted samples were subjected to a column cleanup procedure which removes the interfering chemicals and concentrates the target analytes. The cleanup method usually entails running the sample through a chromatographic column containing a specific adsorbent material. The type of adsorbent used is determined by the contaminants being targeted. The silica gel and activated carbon are all commonly used adsorbents. These materials hold certain chemicals while enabling target analytes to pass through. During the passive air sampling, the column chromatography is an essential key for obtaining effective results in the examination of air samples includes target pollutants. In general, each air samples consists a complicated mixture of contaminants with different chemical characteristics. Due to the similar architectures and the presence of various isomers, PCDDs/Fs and PCBs must be carefully separated.

The sample is put onto the column, and the retained interfering chemicals are washed away by the utilization of appropriate eluent (solvent). The target analytes are still adsorbed on the column. Following elution, the target analytes are extracted from the column by washing them with a different solvent. The analytes' eluate is collected for further analysis. From that, the extracted pollutants are separated into different categories with the help of column chromatography. The sample extracts were separated into four halves, with each quarter undergoing compound-specific cleanup. Through this, the separation of complex mixtures into individual pollutants is enabled in a significant manner. The eluate is concentrated to improve the sensitivity of future analytical procedures.

The separated pollutants (concentrated sample) are examined by using instruments like high-resolution gas chromatography/mass spectrometry (HRGC/MS) to identify and quantify the target pollutants (PCDD/Fs, PCBs, PAEs, DEHA, PAHs). The High-Resolution Gas Chromatography coupled with High-Resolution Mass Spectrometry (HRGC/HRMS) for PCBs and PCDDs/Fs and the Gas Chromatography-Mass Spectrometry (GC-MS) for PAHs, PAEs, and DEHA.

PCDD/Fs- The high-resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS) (JEOL JMS-800D) is utilized for quantifying the PCDDs/Fs and PCBs. To obtain the chromatographic separation, HRGC/HRMS utilized the BPX-DXN (Dioxin related compounds) capillary column from the SGE (30 m × 0.15 mm i.d). The oven temperature for TeCDD/Fs was set at 160°C for 3.15 minutes, then increased to 300°C at a rate of 20°C/min, then to 200°C (0 min hold time) at a rate of 100°C/min at a rate of 10°C/min, and lastly to 265°C. Here, the fixed temperature was increased to 300°C (hold time-10 min), 200°C (hold time-0 min), and then 265°C (hold time-5 min). The oven temperature for PeCDD/Fs and HeCDD/Fs was set to 160°C for 3.15 min, then increased to 200°C at a rate of 20°C/min, then to 240°C, then to 285°C at a rate of 2°C/min at a rate of 5°C/min, and finally to 320°C . Here, the fixed temperature was increased to 200°C (hold time-8 min), 240°C (hold time-1.5 min), 285°C (hold time-0 min), and 320°C (hold time-3 min).

PCBs- The gas chromatograph (Agilent Technologies, USA, 7890B) coupled with mass spectrometer (5977A) were utilized for analysing the PCBs. Helium was employed as the carrier gas at 1.2 mL/min in the constant-flow mode. The oven temperature was started at 100°C for 1 min and increased to 140°C at a rate of 4°C/min, then ramped to 180°C (0 min hold time) at a rate of 20°C/min then to 210°C at a rate of 3°C/min and finally to 290°C at a rate of 8 °C/min. Here, 140°C (hold time-0 min), 180°C (hold time-0 min), 210°C (hold time-0 min) and 290°C (hold time-10 min). A 1µL sample was injected in splitless time after a 5-minute solvent delay. The injector temperature was 250°C. The multi-level calibrations were carried out utilizing PCB mix standards (Cambridge Isotope Laboratories, USA) with a correlation coefficient of R2 > 0.999.

Plasticizers- PAEs and DEHA were examined with the aid of gas chromatograph (Agilent Technologies, USA, 7890B) and mass spectrometer (5977A). A 1µL concentration eluate was injected at 280°C using helium as the carrier gas (1.5mL/min, 99.99% purity). The column temperature program was began at 100°C for 2 minutes, increased to 150°C at a rate of 10°C/min, and then elevated to 300°C at an 8°C/min rate, held for 10 minutes. The mass spectrometer was set to electron ionization (EI) mode at 70eV and emitting at 60µA.

PAHs- PAHs were examined by using a gas chromatograph (Agilent Technologies, USA, 7890B) and a mass spectrometer (5977A). The injector temperature was set at 290°C, and the flow rate was maintained at 1.8mL/min. The initial temperature was kept at 60°C for 1 minute before increasing to 290°C at a rate of 4°C/min and remaining there for 20 minutes.

Quality control- The PUF disks were pre-cleaned, as stated elsewhere. The glass wares were thoroughly cleaned and dried in an oven, followed by a rinse with acetone and hexane before use. The polyurethane foam underwent pre-cleaning through sonication in hexane and acetone for three consecutive 30-minute operations. The polyurethane foams were dried in a desiccator, removing solvent, and then packed in aluminum foil and placed in a plastic bag for sampling. The four field blanks were collected for each city during sampling, with one blank sample analyzed for each set of four samples, following the extraction and column clean up procedure. After deployment, all samples were meticulously packed, transported, and stored at -20°C until further analysis.

DATA ANALYSIS:

This stage incorporates with the concentration estimation and source identification. According to the instrument response and calibration standards, the concentrations of each pollutant in the air samples are determined**.** Then, the data is analyzed for discovering the trends and variations in the pollutant levels across different locations and sectors. Here, the statistical analysis utilizing Trajectory Modeling, Positive Matrix Factorization, and Positive Matrix Factorization are incorporated for pinpointing the major contributors i.e., sectors within the cities.

In this research work, the Trajectory Modeling is designed aimed at comprehending the **dispersion patterns** of pollutants across different sectors in the air by pursuing the movement of air masses over time and space. The use of Trajectory Modeling facilitates the application of source identification, transportation patterns, and distance influence. During Trajectory Modeling, the backward movements of air parcels from sampling locations to potential source regions are tracked. Here, the Trajectory Modeling utilizes the meteorological data (wind speed, direction, temperature, etc.) for the purpose of simulating the air parcel trajectories which reveals the air masses' origins arriving at the sampling site.

Table 2 Meteorological data collected in four cities

Meteorological data	Cities			
	Kanyakumari	Noida	Pune	Mysore
Wind speed (km/hr)	3 km/hr	8 km/hr	7 km/hr	8 km/hr
Temperature (°C)	30°C	16°C	32°C	32°C
Humidity (%)	88%	74%	65%	62%

According to the results of Trajectory Modeling, the **potential source areas** and the **transport pathways** of the pollutants revealed. Besides, it indicates if contaminants are emitted from adjacent or distant sources. Thus, the **intra-urban emission sources** in the four cities of India are determined. The details of the migration of PCDD/Fs, PCBs, PAEs, and PAHs over five various sectors also obtained.

The Positive Matrix Factorization is a multivariate statistical tool utilized in the environmental research with the objective of finding and quantifying the **contributions of different emission sources** to observed pollutant concentrations. In this research work, the Positive Matrix Factorization is utilized in order to detect the potential emission sources of the pollutants. Here, the concentrations of various pollutants (PCDD/Fs, PCBs, PAEs, PAHs, etc.) determined at different sampling locations (five sectors) are taken as input. After this, the observed pollutant concentrations are decomposed into a set of **source profiles** (factors). Each factor represents a specific emission source (five sectors). According to the identified factors, the difference between the observed concentrations and the reconstructed concentrations are reduced. The identified factors helps in identifying which sources contribute most to the observed pollution levels. From this, the dominance of dioxin-like PCBs (dl-PCBs) to combustion as a potential primary source of emissions is discovered. After this, the contributions of different emission sources are quantified to the overall pollutant concentrations that aids in identifying the primary sources of pollution.

The Principal Component Analysis is one of the statistical methods. Finally, the Principal Component Analysis is carried out for obtaining the dimensionality reduction and pattern recognition. The Principal Component Analysis takes the concentrations of pollutants (variables) across different sampling locations as input. Followed by, the data transformation is carried out by converting the original pollutant variables into a set of **uncorrelated principal components**. Each principal component captures a certain amount of variance in the data. According to the amount of variance, the components are ranked in order to detect the influential pollutants. By the performance of the Principal Component Analysis, the common patterns across different pollutants are identified in a significant manner. The pollutants' concentrations are varied depending on the location, season, and specific sampling sites. The concentrations of the target pollutants varied across the sectors as given below.

PCDD/Fs- Ranged from 3.1 to 26pg/m³ (average ± standard deviation: 14 ± 7pg/m³).
PCBs- Ranged from 0.5 to 52ng/m³ (average ± SD: 9 ± 12ng/m³).
Plasticizers (PAEs and DEHA)- Ranged from 7.5 to 520ng/m³ (average ± SD: 63 ± 107ng/m³).
PAHs-Ranged from 6 to 33ng/m³ (average ± SD: 17 ± 6ng/m³).

The electronic waste sector made a large contribution to PCB concentrations (45% of total PCB levels). Dioxin-like PCBs (dl-PCBs), particularly PCB-126, were prevalent, indicating burning as the predominant source of emissions. The electronic waste sector has consistently elevated levels of PCDD/Fs, PCBs, and plasticizers. The industrial sector had the highest levels of PAHs, followed by the electronic waste sector. The electronic waste sector showed the highest levels of toxic equivalents (TEQs) from dl-PCBs, with PCB-126 being the primary contributor. The electronic waste sector (Mysore > Kanyakumari > Noida), both kids and adults were projected to have the highest inhalation hazards from dl-PCBs and plasticizers. From this result, it is clearly known that the electronic waste has a substantial impact on air quality. This report provides a comprehensive analysis of the data, detailing the concentrations of pollutants (i.e., pollutants concentrations at each sampling location), spatial variations in pollutant levels across the cities, and potential emission sources. This research work enables researchers to analyse the air quality and aids in the identification of potential environmental and health hazards linked with these activities.

IV. RESULTS AND DISCUSSION

This research work is focused on four cities in India while selecting five specific sectors within each city. For the purpose of performing air monitoring, this research work utilizes the PUF disk as the passive air sampling medium. These passive air samplers with PUF are employed at each sector for collecting the target pollutants from the ambient air environment. This research work conducts passive air sampling over a specific period of time. Followed by, the concentrations of the target pollutants are determined. Then, the **Trajectory modeling** and **positive matrix factorization are utilized for** attributing the intraurban emission sources. Finally, the contribution of various sectors to total pollutant concentrations are identified in an effective manner. The highest concentrations of PCDD/Fs, PCBs, and plasticizers (PAEs) are exhibited in the electronic waste sector. The maximum PAH concentrations are occurred at the industrial sector. The electronic wastes sector in Mysore followed by Kanyakumari and Noida exhibited the highest risks for dl-PCBs and plasticizers. PCDD/Fs compounds are extremely hazardous and POPs. PCBs are recognized to have negative impacts on human health and the environment. PAEs are frequently utilized in plastics and can leach into the environment. PAHs are associated with combustion processes and may cause health hazards. These contaminants have consequences for human health and the environment.

SAMPLING METHOD:

This research work utilizes the passive air sampling with PUF disks.

SAMPLING LOCATIONS:

This research work considers four cities (**Kanyakumari, Noida, Mysore** and **Pune**) of India and five sectors (**Electronic Waste, Information Technology, Industrial, Residential** and **Dumpsites)** in each city.

ANALYSIS OF POLLUTANTS:

This research work performs air monitoring by examining the four pollutants in the air such as PCDD/Fs (polychlorinated dibenzo-p-dioxins and furans), PCBs (polychlorinated biphenyls), PAEs (phthalate esters) including DEHA (bis-(2-ethylhexyl) phthalate) and PAHs (polycyclic aromatic hydrocarbons)

CONCENTRATION MEASUREMENT:

In this research work, the **c**oncentrations of target pollutants were reported in pico grams per cubic meter (pg/m³) for PCDD/Fs and nano grams per cubic meter (ng/m³) for PCBs, PAEs and PAHs.

SOURCE IDENTIFICATION:

This research work utilizes the Trajectory Modeling and Positive Matrix Factorization, and Principal Component Analysis to estimate and attribute sources of target pollutants within the city along sectors.

LEVELS OF TARGET POLLUTANTS:

PCDD/Fs **(Polychlorinated Dibenzo-p-dioxins and Furans)-** The concentrations of PCDDs in major cities of India is ranged from 1.2 to 21.3pg/m³, while PCDFs is ranged between 1 and 5.8pg/m³.
PCBs (Polychlorinated Biphenyls)- The total concentration of 25 PCB varied significantly, ranging between 0.5 and 52ng/m³ .
Plasticizers (PAEs and DEHA)- The total concentrations of six PAEs and DEHA ranged between 7.5 and 520ng/m³.
PAHs (Polycyclic Aromatic Hydrocarbons)- The total concentration of 15 priority PAHs listed by the US Environmental Protection Agency varied between 6.2 and 33ng/m³.

Table 3 Percentage Distribution of Pollutants

SECTORS	PERCENTAGE DISTRIBUTION OF POLLUTANTS			
	PCDD/Fs	PCBs	PLASTICIZERS	PAHs
ELECTRONIC WASTE	58	44	55	29
INFORMATION TECHNOLOGY	32	15	22	14
INDUSTRIAL	8	7	4	16
RESIDENTIAL	13	21	17	33
DUMPSITE	4	13	3	9

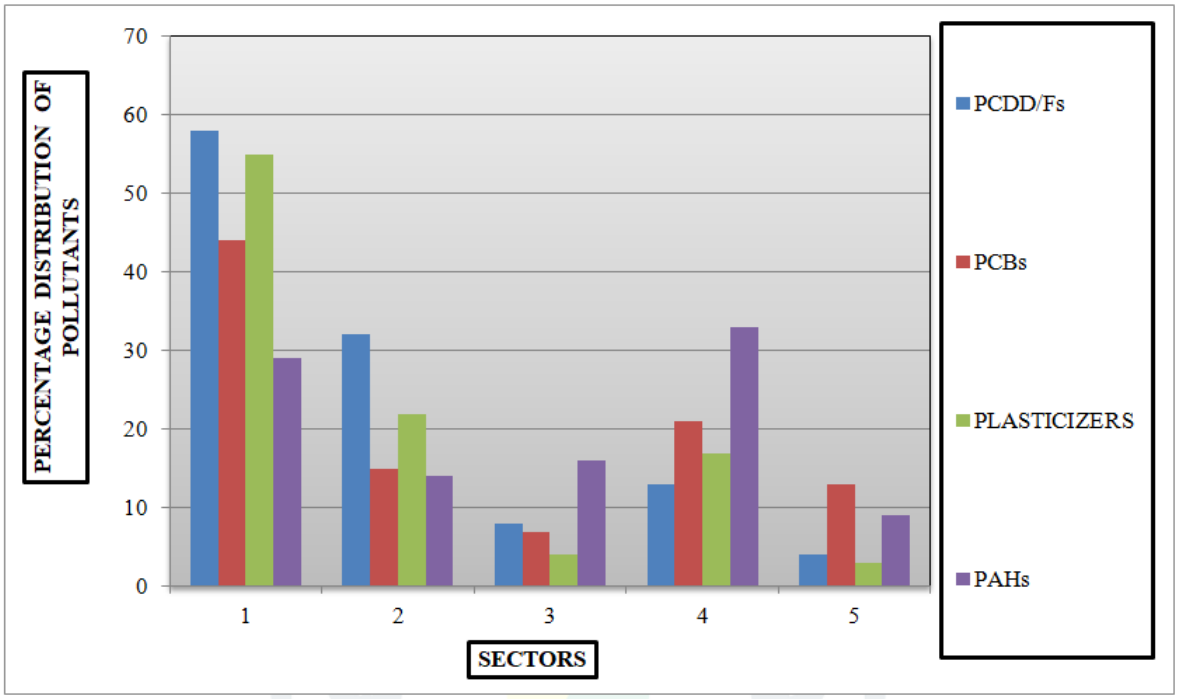

Figure 4 Graphical representations for percentage distribution of pollutants

As shown in table 3 and figure 4, the informal electronic waste recycling is a significant source of air pollution with PCDDs/Fs, PCBs, and plasticizers**.** The concentrations of these pollutants were consistently higher near informal recycling sites compared to other investigated areas**.** The combustion processes used during informal e-waste processing likely contribute to PCDD/F and PCB emissions. The specific homologue profiles of these pollutants pointed towards combustion as a major source. The industrial areas are the primary source of PAH air pollution. While e-waste sites also contribute to PAHs, their levels were lower compared to industrial zones.

V. CONCLUSION

The passive air sampling is a valuable method in order to monitor the environmental pollutants. The research work performs air monitoring for identifying the source of pollutants by implementing the passive air sampling technique with multi-step process involves passive air sampling followed by effective analysis techniques. The research work conducts the inquiry by deploying passive air samplers with PUFs throughout cities to gather pollutants over a set length of time. This enables long-term monitoring without requiring regular on-site attendance. After the sampling period, the samplers are collected and the captured pollutants are extracted using solvents. The extracted samples then underwent analysis using advanced techniques Gas Chromatography/Mass Spectrometry (GC/MS) for identifying the individual pollutants regarding chemical properties. It allows for quantification of POPs present in the sample. Followed by the Trajectory Modeling for data analysis and Positive Matrix Factorization and Principal Component Analysis for source apportionment are implemented. The Trajectory Modeling identifies the potential source regions. The Positive Matrix Factorization and Principal Component Analysis pinpoint the major sources contributing to the observed air pollution levels.

As discussed above, this research work successfully assess the POPs in four Indian cities like Kanyakumari, Noida, Mysore, and Pune with five specific sectors such as electronic waste, information technology, industrial, residential and dumpsites. In this research work, the concentrations of POPs including PCDD/Fs, PCBs, Plasticizers (PAEs and DEHA), and PAHs were determined. The sum of 17 PCDD/Fs ranged from 3.1 to 26pg/m³ (average ± standard deviation: 14 ± 7 pg/m³). The sum of PCBs ranged from 0.5 to 52ng/m³ (average ± SD: 9 ± 12ng/m³). The total concentration of six PAEs and DEHA ranged from 7.5 to 520ng/m³ (average ± SD: 63 ± 107ng/m³). The sum concentrations of 15 PAH ranged from 6 to 33ng/m³ (average ± SD: 17 ± 6ng/m³). This research work is successfully detected the concerning levels of various pollutant in the air environment. This research work shows that the informal electronic waste recycling is a substantial source of air pollution in Indian cities.

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