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The Fresh Air Wristband: A wearable air pollutant sampler

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Abstract

Evaluation of cumulative exposure to air pollutant mixtures has been challenged by traditional techniques due to the weight, limited battery life, and cost. The performance of a novel wearable air pollutant sampler, the Fresh Air wristband, to passively concentrate nitrogen dioxide (NO_2), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) was investigated. The Fresh Air Wristband consisted of a commercially-available triethanolamine-coated pad to collect NO_2 and polydimethylsiloxane (PDMS) sorbent bar to sample VOCs and PAHs. Concentrations were measured off-line following the assessment period. The repeatability and rate of VOC and PAHs uptake by the PDMS sorbent bar was evaluated and the Fresh Air wristband was tested as exposure tool. The PDMS sorbent bar achieved reproducible uptake of from ambient air with uptake rates varying from 2 to 5 days across compounds. Higher molecular weight compounds (>180 g/mol) were well retained in the PDMS sorbent bar over multi-day periods. The Fresh Air wristband was demonstrated as a personal exposure tool; exposures of school-aged children were found to differ by sex, asthma status, home kitchen characteristics, and mode of travel to school. The lightweight, wearable Fresh Air wristband will enable future longitudinal air pollutant exposure assessment in vulnerable populations.

Keywords: personal exposure assessment, polycyclic aromatic hydrocarbons, children, asthma

INTRODUCTION

Organic air pollutants, such as volatile organic compounds (**VOCs**) and polycyclic aromatic hydrocarbons (**PAHs**), are released from various sources, including combustion activities (cooking, cigarette smoke, candles/incenses, heating) as well as evaporation from personal care, cleaning products, and building materials[1-3]. Exposure has been associated with respiratory and cardiovascular disease as well as reproductive and neurobehavioral outcomes[4-7]. Personal air pollutant monitoring systems traditionally include backpacks containing expensive hand-held air monitors and filters/pumps[8-10]. Pollutants sampled onto filters are typically solvent extracted and analysed by gas chromatography mass spectrometry (**GC-MS**)[11]. This sample preparation approach is laborious, limiting the feasibility of evaluating personal exposure on a larger scale. Alternative assessment approaches are necessary to study longitudinal environmental exposures of vulnerable populations[12-14].

Passive sampling approaches have been used to measure ambient concentrations of VOCs[15, 16], PAHs[17-20], phthalates[21], flame retardants[22] and pesticides[23, 24] at stationary monitoring locations. This type of sampler operates without a pump and is comprised of a polymeric sorbent (*i.e.*, polydimethylsiloxane, **PDMS**; activated carbon; divinylbenzene; carboxen; polyethylene) which acts an extraction phase for airborne organic pollutants[25]. The rate of pollutant initially extracted from the air by the sorbent membrane is proportional to ambient concentrations (*linear regime*). As the sampling time is extended, uptake of air pollutants by the sorbent membrane continues until an equilibrium is reached with ambient concentrations (*near equilibrium regime*) (See review by Poole et al.[26]). Restricting sorbent membrane extraction to the linear regime enables a time-weighted average exposure concentration to be determined[27, 28]. The extraction selectivity as well as rate and capacity are determined by the volume and geometric configuration of the sorbent membrane as well as the agitation conditions of the sampler (*i.e.*, boundary layer thickness)[29-31].

Sorbent membranes have been incorporated into wearable form factors to facilitate personal exposure assessment. Badges/brooches and diffusion tubes worn on an individual's lapel have been deployed to evaluate VOC[32-34] and SVOC[35] exposure. Several studies have recently demonstrated the utility of commercially-available silicone wristbands (24hourwristband.com; wristbands.com) for sampling SVOCs[36-38]. The feasibility of detecting an individual's environmental and occupational pollutant exposures using these silicone wristbands has been reported for various locations (U.S.[19, 38, 39], Chile[40], Peru[41], Senegal[42]) for multi-hour to multi-week exposure assessment periods[43]. These wristbands have also been deployed with pre-school children to assess exposure concentrations of polybrominated diphenyl ethers and organophosphate flame retardants[44] and adults to evaluate exposure to pesticide residues[45, 46]. Measured diphenyl ethers and organophosphate flame retardants and pesticides have been reported to be correlated with their respective biomarkers in serum[47], urine[48] or hair[49]. PAHs exposure across a cohort of pregnant women have further been positively correlated with PAH concentrations measured using traditional active sampling monitors as well as urinary levels of PAH metabolites[13].

While commercially-available silicone wristbands have emerged as an attractive exposure assessment tool for a range of organic exposures, it is important to acknowledge the multiple exposure routes captured by tool as well as challenges with the current wristband analysis approach. This wristband is comprised of a ~2.5 mm thick silicone sorbent membrane. As this sorbent membrane is in contact with the air and skin during the assessment period, the

measured exposure represents a combination of ambient air and dermal sources. Application of lotions by individual to their hands/arms, may create a film on the wristband surface which may impact the uptake rate/capacity of environmental contaminants from other sources. Regarding analysis methods, current wristband protocols use a solvent extraction method. This manual procedure requires extended laboratory personnel time, limiting the feasibility of the silicone wristbands in larger study populations. Understanding the implications of the wristband design on exposure estimates as well as the feasibility of the analysis workflow are critical as the deployment of wearable passive samplers in epidemiology studies increases.

We present a novel wearable sampler, the Fresh Air wristband, to characterise personal air pollutant exposures (**Figure 1A**). This sampler was designed to exclusively evaluate contaminant exposure through inhalation and use a solvent-free extraction protocol with the aim of increasing analysis throughput. The Fresh Air wristband consisted of a polytetrafluoroethylene (**PTFE**) chamber that contained two passive sampling devices: a PDMS sorbent bar which absorbed airborne organic pollutants and a commercially-available Ogawa pad for sampling nitrogen dioxide ($\mathbf{NO_2}$). The wristband was worn and then returned to the laboratory for analysis. The objectives of this study were to (1) demonstrate VOCs and PAHs uptake repeatability and rate by the PDMS sorbent bar, (2) evaluate the stability of absorbed compounds in the PDMS sorbent bar, and (3) demonstrate application of this Fresh Air wristband as a personal exposure assessment tool for NO_2 and airborne organic pollutants.

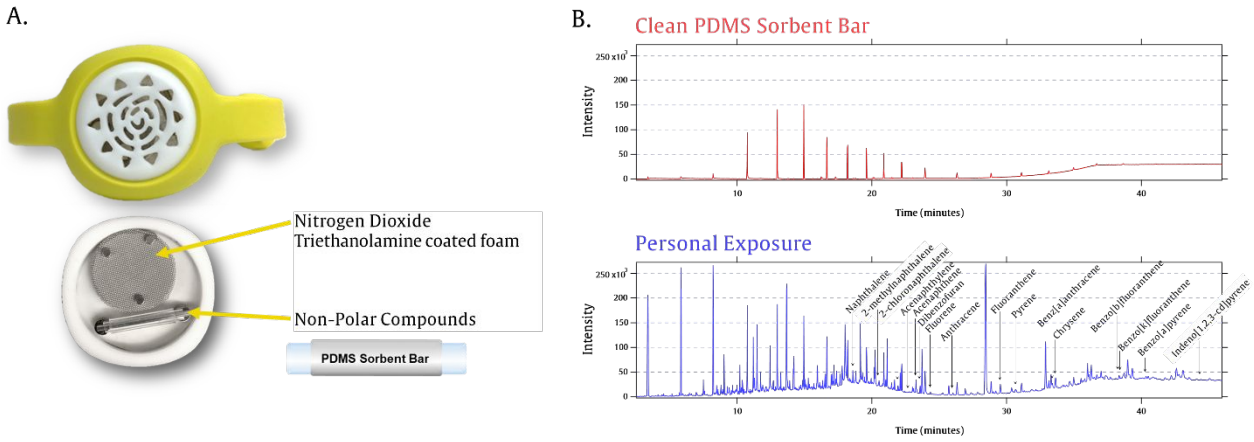

Figure 1. ***The Fresh Air Wristband Passive Sampling Device.*** A) This wristband can be used to evaluate personal inhalation exposure to non-polar airborne chemicals using a PDMS sorbent bar and nitrogen dioxide using a commercially-available Ogawa pad. B) Total ion chromatograms of a clean PDMS sorbent bar (top) and a PDMS sorbent bar worn for 24 hours in the Fresh Air wristband (bottom). Observed peaks in the clean bar chromatogram were confirmed as siloxane. Peaks corresponding to PAHs are labelled for the personal exposure chromatogram.

METHODS AND MATERIALS

PDMS Sorbent Bar and Fresh Air Wristband Preparation and Analysis.

PDMS sorbent bars were analysed by thermal desorption GC time-of-flight MS for VOC and PAHs. Ogawa pads were analysed for NO_2, following the manufacturer's protocols; these methods have been previously validated and used widely for NO_2 monitoring[50-52]. Details for are included in the Supporting Information (**SI**).

Evaluation of the PDMS Sorbent Bar for Air Pollutant Sampling.
To evaluate the PDMS sorbent bar as a passive sampler, the repeatability of air pollutant uptake was tested. The uptake rate of these compounds from ambient air was also assessed in addition to the ability of the PDMS sorbent bar to retain these air pollutants over an extended exposure assessment period. See the SI for more details.

Application of the Fresh Air Wristband as a Personal Exposure Assessment.
A PDMS sorbent bar and Ogawa pad were mounted into the Fresh Air wristband using forceps immediately prior to the deployment. These sampling matrices were removed from the wristband at the end of the exposure assessment period and stored in air-tight amber glass vials until analysis. The wearability during typical daily activities of this sampling device was evaluated by adult participants over a 24-hour period. The Fresh Air wristband was additional tested for quantitative personal exposure assessment with children (12-13 years) over 4.3 days. Children lived in Springfield, MA and attended the same school. Differences by sex and asthma status as well as home and travel characteristics were compared. Further details can be found in the SI.

RESULTS AND DISCUSSION

Laboratory Calibration of the PDMS Sorbent Bar for Quantifying VOCs and PAHs.
The feasibility of quantifying exposures was initially evaluated. PDMS sorbent bars were infused with a mixture containing known concentrations of VOCs and PAHs and used to prepare six-point calibration curves. Calibration curves were linear for all analytes (R^2 range: 0.982-1.000; **Table S1**). Across five replicates at three concentrations (375, 750, 1500 pg), the lowest average coefficient of variation was found for acenaphthene (3.3%, range: 1.2-5.6%) and the highest was observed for chrysene (11.4%, range: 11.2-11.6%).

Field Evaluation of the Repeatability of Uptake by the PDMS Sorbent Bar.
The repeatability of airborne VOCs and PAHs uptake by the PDMS sorbent bar was assessed in an industrial kitchen (**Figure S3**). All but six lower molecular weight compounds were detected. The average coefficient of variation across detected analytes was 4.1% (range: 0.2-10.3%) (**Table S1**).

Field Evaluation of Uptake Rate by the PDMS Sorbent Bar.
PDMS sorbent bars were placed in Fresh Air wristbands and positioned at a stationary indoor sampling location with stable temperature (23°C) and air movement (<0.025 m/s). Pollutant uptake was initially linear and continued until equilibrium was reached with ambient air concentrations. The length of time to attain equilibrium differed across compounds and is shown for three compounds in **Figure 2A**. As the mass loading in this sampling regime is proportional to air concentrations and is useful in guide, it was of interest to determine the duration of linear uptake for each compound to guide the length of the exposure assessment period. The length of the linear regime ranged from <2 to 5 days for all measured VOCs and PAHs (**Figure 2B, Table S2**). The sampling rate of the PDMS sorbent bar was calculated as the slope in the linear uptake period. Uptake rates ranged from 0.01 to 4.06 pg/hour (**Table S2**) and are shown for three PAHs in **Figure 2C**.

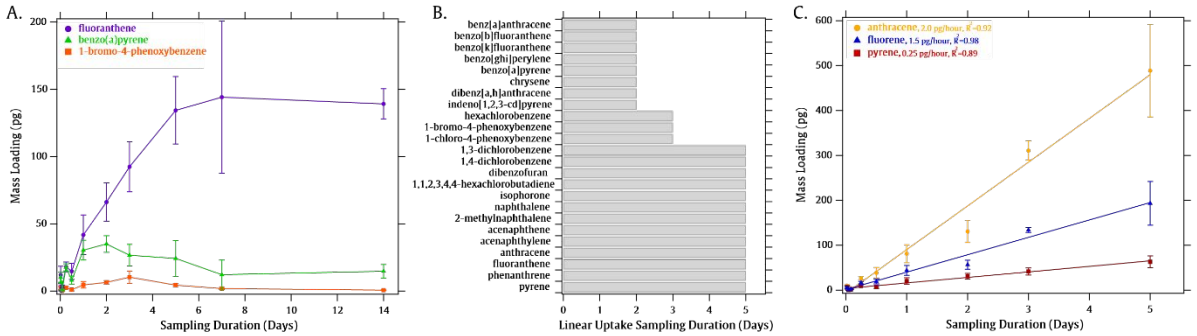

Figure 2. ***PDMS sorbent bar uptake of VOCs and PAHs from an indoor environment for PAHs and VOCs.*** A) Measured uptake (mean ± standard deviation) of three compounds with variable times to reached equilibrium over the 14-day study period. B) Length of the linear uptake regime for measured VOCs and PAHs. C) Comparison of linear uptake rates for three prevalent PAHs.

Laboratory Evaluation of Pollutant Stability on the PDMS Sorbent Bar.
As the Fresh Air wristband was designed to be worn over multi-day exposure periods, it was of interest to evaluate the stability of absorbed compounds in the PDMS sorbent bar. PDMS sorbent bars in the Fresh Air wristband were infused with deuterated internal standards and kept at 23 ºC or 4 ºC for 24 hours. Lower molecular weight compounds (<180 g/mol) experienced losses following 24 hours at 23 ^{0}C compared to 4 ^{0}C (**Figure S3**); losses for these lighter compounds were proportional to molecular weight (R^2=0.905). Retention of higher molecular weights (>180 g/mol) in the PDMS sorbent bar were not influenced by temperature.

Application of the Fresh Air Wristband as a Personal Exposure Tool.
Adult participants evaluating the wearability of the Fresh Air wristband reported this exposure assessment tool could be worn during all daily activities and was only removed while bathing or swimming. These 24-hour personal exposure samples demonstrated analytes were passively absorbed by the PDMS sorbent bar. An example of one personal exposure sample is shown in **Figure 1B**. These chemical features were not detected in clean PDMS sorbent bars following thermal conditioning.

The Fresh Air wristband was also evaluated a tool for quantitative exposure assessment in a pilot study of children. Wristbands were worn for 4.3 days and placed proximal to their bed overnight. Three wristbands were not returned for analysis; the presented exposure analysis is for 33 participants (**Table S3**). All children attended the same school and had similar sociodemographic factors. Participants were predominately girls (69%) and 33% had physician diagnosed asthma. It should be noted that we did not target children with asthma to participate in this study; however, were interested in evaluating exposure differences between children with and without asthma given the strong evidence supporting the association between air pollution and asthma morbidity in children[53-61]. We were motivated to conduct the study in Springfield, MA given the high prevalence of childhood asthma (17%) to the state-wide rate (11%)[62].

Nineteen percent of children lived with a smoker and their house was fit with either an electric (56%) or gas stove. Most reported use of a stove top ventilation hood while cooking (69%). Children all attended the same school and the average daily round-time commute time was 61

minutes (SD=36 minutes). Children were either driven to school (44%) or commuted by a combination or walking and bus.

Elevated exposure concentrations were found for girls compared to boys for total PAHs as well as individual PAHs, including benzo[k]fluoranthene and anthracene; no difference was found for other compounds (**Figure 3A, Table S4)**. Children with physician diagnosed asthma were found to have elevated personal exposure concentrations of pyrene and acenaphthylene compared to children with no reported asthma diagnosis (**Figure 3B, Table S5**). These results do not support a causative role of these exposures for risk of asthma development. Rather, results are presented to highlight that increased exposure levels of these pollutants may exacerbate existing asthma. Specific PM components with pro-oxidant capabilities (i.e. VOCs, PAHs) can induce oxidative stress and contribute to the pathogenesis and/or exacerbation of asthma[63]. Studies have evaluated PAH exposure in relationship to asthma outcomes, most have used stationary samplers placed at the child's home or assessed PAH metabolites in urine. Few other studies have directly measured personal exposure to PAH in relationship with asthma outcomes due to challenges with exposure assessment. Results from the current study demonstrate the utility of the Fresh Air wristband as a wearable air pollutant sampler for exposure assessment of paediatric populations.

Exposure to emissions from traffic[64] and cooking, specifically gas stoves[65, 66], have been associated with asthma outcomes in children. Thus, exposure concentrations measured in the current study were compared for children with different home characteristics or school commutes. Children living in houses with gas stoves were found to have increased levels of total PAHs as well as several individual PAHs, including pyrene, benz[a]anthracene, benzo[k]fluoranthene, chrysene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene compared to electric stoves (**Figure 3C, Table S6**). In households with gas stoves which reported use of the stove ventilation hood (duct or ductless design), decreased personal NO_2 exposure concentrations were observed, compared to families which did not used a vent (**Figure 3D, Table S7**). Similar trends were also found for indeno[1,2,3-cd]pyrene. Different modes of commuting were further associated with different exposure concentration: car commuters exhibited increased anthracene and phenanthrene compared to travel by bus/walking. (**Figure 3E, Table S8**). These findings are supported by a recent review reporting commuting by car was associated with elevated exposures (PM mass and number concentration, black carbon) compared to bus commuters and active modes of transport[67, 68].

The Fresh Air wristband was developed with the objective of characterising cumulative personal exposure to air pollutant mixtures. NO_2 was passively sampled with an Ogawa pad and VOCs and PAHs were collected using a PDMS sorbent bar. While the NO_2 measurements using commercially-available Ogawa pads have been well described in the literature[51, 52, 69, 70], this is the first study to evaluate airborne VOC and PAH sampling by a PDMS sorbent bar mounted in a wearable device.

Good reproducibility was found for all compounds but only higher molecular weight PAHs (>180 g/mol) were well retained in the PDMS sorbent bar for sampling periods >24 hours at room temperature. Further stability testing over extended periods and additional temperatures is the subject of our future studies. The current study was limited in the evaluation of the PDMS sorbent bar compared with other exposure assessment methods.

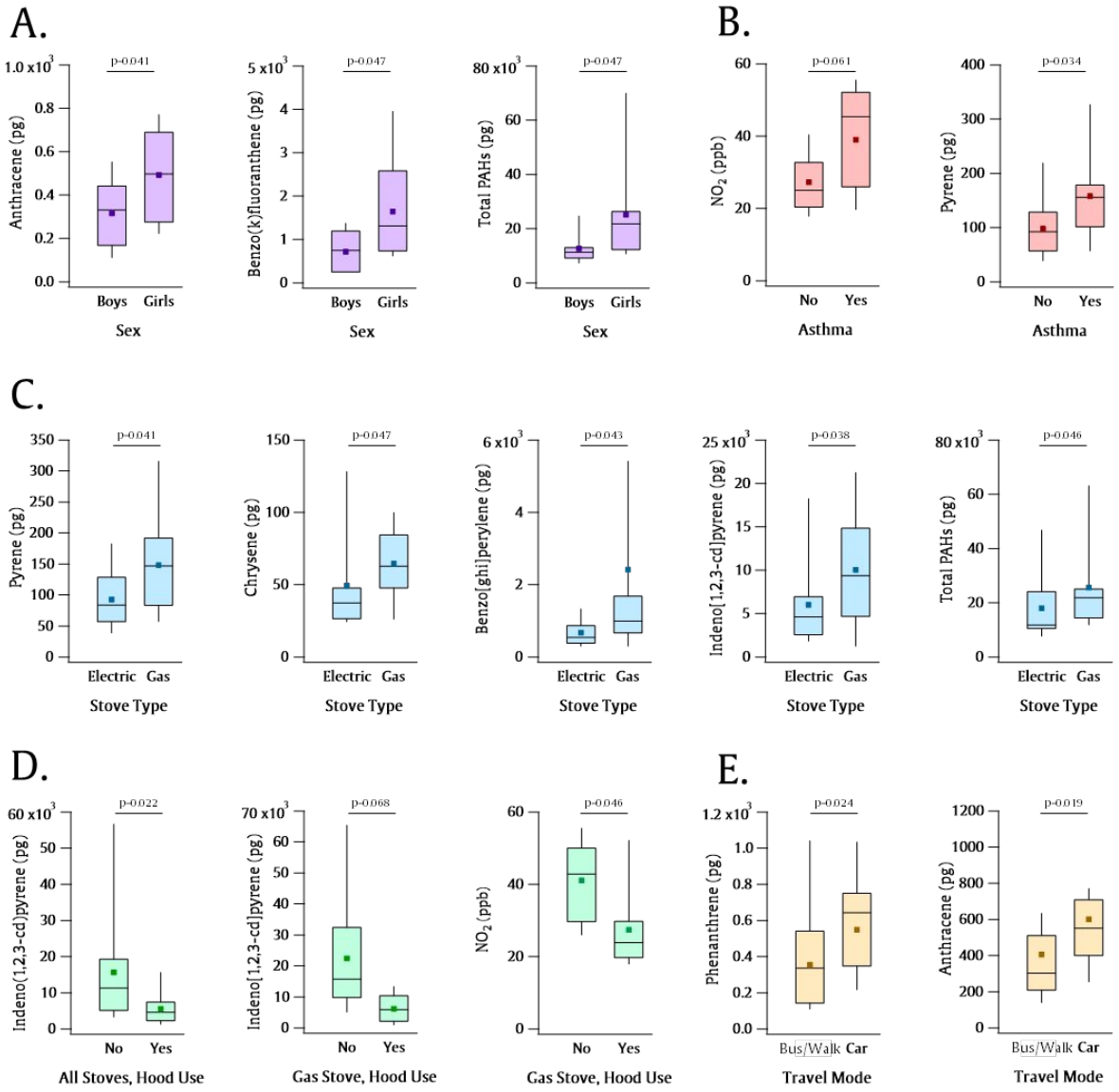

Figure 3. ***Personal exposure assessment of children using the Fresh Air wristband.*** Comparison of exposure levels by sex (boys n=10, girls n=23), asthma status (no=22; yes=11), stove type (electric=18; gas=15), ventilation hood use in homes with gas stoves (no=8; yes=7), home-to-school mode of travel (bus/walk=18; car=15).

The Fresh Air wristband was demonstrated as a personal exposure tool with school-aged children. Atmospheric concentrations were reported for NO_2 using a commercially-available passive sampler while exposure VOCs and PAHs levels were reported as mass uptake on the PDMS sorbent bar. The reported mass loading of lower molecular weight compounds likely reflected exposures levels over the past 24 hours rather than cumulative exposure of the multi-day assessment period given the limited retention in the PDMS sorbent bar. Children's exposures were found to differ across sex, asthma status, home kitchen characteristics, and

mode of travel to school. The number of participants in the current study was limited and results should be interpreted accordingly.

Use of the Fresh Air wristband in prospective epidemiological studies has the potential to provide insight into an individual's unique pollutant profiles. This sampling technique will further enable deployment across large populations, increasing the quantity of environmental data available for evaluating environmental risk factors for disease.

The authors declare no competing financial interest.

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Supporting Information

Method information regarding Fresh Air wristband preparation, analysis, validation, and personal exposure assessment. Additional results detailing the analytical method (Figures S1, S2; Tables S1, S2), wristband sampling performance (Figure S3), and personal exposure concentrations of children in Springfield, MA (Tables S3-S8).

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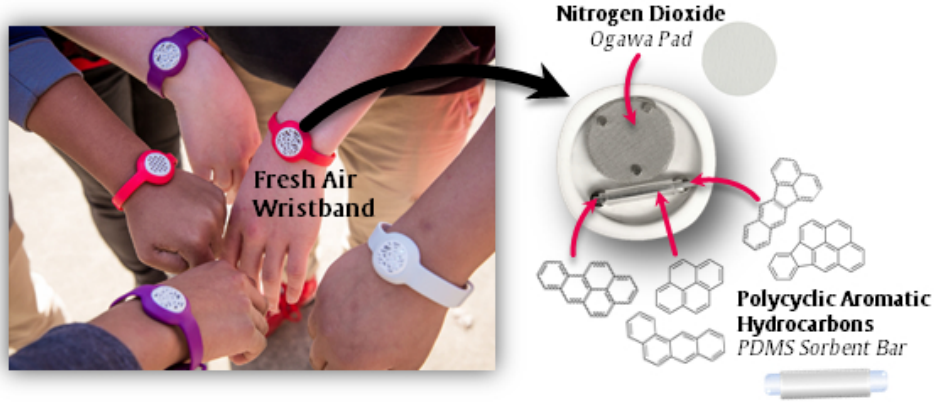

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