



Assessment of exposure of gas station attendants in Sri Lanka to benzene, toluene and xylenes

Paul T.J. Scheepers^{a,*}, Laurie de Werdt^{a,1}, Maurice van Dael^a, Rob Anzion^a, Jeroen Vanoirbeek^b, Radu Corneliu Duca^b, Matteo Creta^b, Lode Godderis^{b,c}, D.T.D. Warnakulasuriya^d, Niranga Manjuri Devanarayana^d

^a Radboud Institute for Health Sciences, Radboudumc, Nijmegen, the Netherlands

^b Centre for Environment and Health, KU Leuven, Leuven, Belgium

^c IDEWE, External Service for Prevention and Protection at Work, Heverlee, Belgium

^d Faculty of Medicine, University of Kelaniya, Thalagaolla Raod, Ragama, 11010, Sri Lanka

ARTICLE INFO

Keywords:

Gasoline
Occupational hygiene
Volatile organic compounds
Urine
Exhaled air

Exposure to benzene, toluene and p-, m-, o-xylene (BTX) was studied in 29 gas station attendants and 16 office workers in Sri Lanka. The aim of this study was to assess the exposure level and identify potential exposure mitigating measures. Pre- and post-shift samples of end-exhaled air were collected and analysed for BTX on a thermal desorption gas chromatography mass spectrometry system (TD-GC-MS). Urine was collected at the same timepoints and analysed for a metabolite of benzene, S-phenyl mercapturic acid (SPMA), using liquid chromatography-mass spectrometry (LC-MS). Environmental exposure was measured by personal air sampling and analysed by gas chromatography flame ionization detection (GC-FID). Median (range) breathing zone air concentrations were 609 (65.1–1960) $\mu\text{g}/\text{m}^3$ for benzene and 746 (< 5.0–2770) $\mu\text{g}/\text{m}^3$ for toluene. Taking into account long working hours, 28% of the measured exposures exceeded the ACGIH threshold limit value (TLV) for an 8-h time-weighted average of 1.6 mg/m^3 for benzene. Xylene isomers were not detected. End-exhaled air concentrations were significantly increased for gas station attendants compared to office workers ($p < 0.005$). The difference was 1-3-fold in pre-shift and 2-5-fold in post-shift samples. The increase from pre-to post-shift amounted to 5-15-fold ($p < 0.005$). Pre-shift BTX concentrations in end-exhaled air were higher in smokers compared to non-smokers ($p < 0.01$). Exposure due to self-reported fuel spills was related to enhanced exhaled BTX ($p < 0.05$). The same was found for sleeping at the location of the gas station between two work-shifts. Benzene in end-exhaled air was moderately associated with benzene in the breathing zone ($r = 0.422$; $p < 0.001$). Median creatinine-corrected S-phenyl mercapturic acid (SPMA) was similar in pre- and post-shift (2.40 and 3.02 $\mu\text{g}/\text{g}$) in gas station attendants but increased in office workers (from 0.55 to 1.07 $\mu\text{g}/\text{g}$). In conclusion, working as a gas station attendant leads to inhalation exposure and occasional skin exposure to BTX. Smoking was identified as the most important co-exposure. Besides taking preventive measure to reduce exposure, the reduction of working hours to 40 h per week is expected to decrease benzene levels below the current TLV.

1. Introduction

In road traffic incomplete combustion of fossil components contributes to air pollution in densely populated cities, which has a profound impact on air quality (Stojić et al., 2015; Raysoni et al., 2017). The use of fossil fuels also leads to occupational exposure during production, transportation and retail primarily at gas stations (IARC, 2014). In Sri Lanka the number of gas stations is 1,200 and employ

between 10,000 and 15,000 gas station attendants. Nowadays, modern gas stations often use a self-service system where the customer is filling up the tank. In these cases, fuel vapours are often scavenged with a built-in vapor recovery system (Eghehi et al., 2000; Eghehi et al., 2002). This protects the customer from inhaling volatile organic compounds (VOC) and also reduces environmental emissions from fuel stations. In Sri Lanka fuel refilling involves a gas station attendant who is expected to have frequent exposure to vapor streaming from the tank

* Corresponding author.

E-mail address: paul.scheepers@radboudumc.nl (P.T.J. Scheepers).

¹ contributed equally.

when the fuel entering the tank pushes out the saturated vapor. If a 60 L tank is still containing 10 L of fuel residue an equivalent volume of 50 L of saturated vapor remains in the tank. When the tanks opened and is filled up, this volume of gasoline vapor will be pushed out of the tank and be dispersed in the ambient air in close range to the gas station attendant. In countries such as Sri Lanka, pumps are often not yet equipped with vapor recovery systems. This, combined with high ambient temperatures and insufficient personal protection may lead to a situation where workers of gas stations receive elevated exposure to fuel vapours (Tunsaringkarn et al., 2012; Zoleikha et al., 2017). Working as a gas station attendant was associated with a range of health effects including lung function changes (De Oliveira et al., 2007; Jo and Song, 2001; Kitwattananavong et al., 2013; Majumdar et al., 2008; Hulke et al., 2012).

Benzene, toluene and ortho-, para-, and meta-xylene (BTX) represent the most abundant aromatic hydrocarbons in gasoline fuel. BTX serves as a proxy for exposure to gasoline and diesel fuel (see Edokpolo et al., 2014 for an overview). These compounds are known for their neurotoxicity which may lead to severe irreversible neurobehavioral impairments known as toxic encephalopathy at high exposures. Benzene is classified as a confirmed risk factor for cancer and implicated in a variety of haematological diseases, including aplastic anaemia, acute myeloid leukaemia and myelodysplastic syndrome (Gross and Paustenbach, 2018). Of all work-related to dispensing of fuel for road vehicles, gas station attendants were implicated with the highest risk for cancer due to benzene exposure. For a lifetime exposure as gas station attendant a cancer risk of 670×10^{-6} was calculated (Edokpolo et al., 2014). In 16.6% of Brazilian workers with an average work history of 16 y of work as gas station attendant, chromosomal abnormalities, mostly translocations, were observed (Santiago et al., 2014). Similar findings were reported in other studies (Tunsaringkarn et al., 2011; Saleem et al., 2018).

The Ceylon Petroleum Corporation (Ceypetco) declared a benzene content of < 1.0% v/v for gasoline 95 oct (equivalent to EURO-4) and < 2.5% v/v for 92 oct gasoline (Ceypetco, 2019). In Sri Lanka fuel adulterity was reported up to 48% for gasoline from 10 gasoline stations in and around Colombo and indicates possible deviations from these specifications (Kulathunga and Mahanama, 2013).

In the present study we investigated gas station attendants in comparison to office workers for exposure to BTX. We collected personal air samples in the breathing zone and verified to what extent the use of passive samplers provides results comparable when using the well-accepted standard of active sampling. In addition, we used an established metabolite of benzene in urine as a biomarker of exposure. We also piloted end-exhaled air collection as a relative new non-invasive approach to biomonitoring of highly volatile substances (Amorim and Cardeal, 2007; Caro and Gallego, 2009). These biomarkers reflect uptake integrated over different time frames and from different routes of exposure and sources of BTX exposure. We also used a newly developed video system to study peak exposures. We aimed to study the exposure of gas station attendants and identified potential mitigating measures to reduce exposure.

2. Materials and methods

For this study, medical ethical approval was obtained from the Ethical Review Board of the medical faculty of the University of Kelaniya, Sri Lanka.

2.1. Study population and person characteristics

Gas station attendants were recruited from four petrol stations (P1 – P4) located in the Gampaha District in the western part of Sri Lanka, northwest of the capital of Colombo (Fig. 1). At the gas station workers rotated in different shifts to ensure a 24/7 service. This resulted in long working hours of 8–16 h (in P2, P3 and P4), depending on the petrol

station. Rest hours also varied from one to two days-off per month in P1 to two weeks of 16 h shifts alternating with two weeks off. Control persons were recruited among males for office work employed at the Colombo North Teaching Hospital. All participants received information about the study and their role and contribution to the study and signed an informed consent form.

All participants were interviewed using a structured questionnaire covering general information, including demographic characteristics, education, occupational history, dietary habits, smoking, alcohol use and other life style factors. If the workers confirmed to consume alcoholic beverages we asked about the number of consumptions per week and also registered the last consumption by calendar date. Specific questions were asked related to chemical exposures at work and exposures from off-work activities and potential sources of exposure at home. In addition to the questionnaire, the gas station attendants were asked to keep a diary and report on the occurrence of fuel spills leading to potential contamination.

2.2. Video imaging of work tasks

To evaluate tasks with peak exposures, video recordings were made using Video Imaging and Data Interfacing and Analysis (VIDITA, 2010). With this software application video images of work tasks were combined with the results of real-time measurements, following the principle of worker's participation (Rosén et al., 2005). The method can be used to make workers aware and to educate and discuss how work practices influence exposure. For this study, real-time measurements were conducted with a MiniRAE 2000 which uses a photo-ionization detector (PID) equipped with a 10.6 eV UV source (RAVEBO, Brielle, The Netherlands) to detect the fuel vapours in the breathing zone (Fig. S1). The signal was sent wireless from a sender that was carried together with the PID to a receiver by Zigbee LAN 2.4 GHz signal connected to a standard notebook computer with the Labview-based software application TestOrganizer v20.6 (TestOrganizer) to visualize the video images synchronized with the real-time exposure monitoring signal from the PID.

2.3. Collection of personal air samples

During the shift, inhalation exposure was studied by collection of personal air samples in the breathing zone. We used a system of passive personal air sampling (PPAS) and, in addition, in 25% of the workers this was combined with active personal air sampling (APAS). For PPAS we used diffusive air samplers with 400 mg of coconut shell coal (Orsa-5, Dräger, Lübeck, Germany). The diffusive badges were taken from the sealed package at the start of the work shift and attached to the work clothes in the breathing zone (Fig. S2). At the end of the shift, the badge sampler was placed back in a gastight container. In gas station attendants, three 6–8 h shift samples were collected on three consecutive workdays. In control persons, an 8 h shift sample was collected on one day. APAS was performed using air suction pumps (Buck Basic 5, A.P. Buck, Orlando, FL, USA or Gillian GilAir, Sensidyne, St Petersburg, FL, USA). Air was drawn through a tube containing activated charcoal adsorbent (Anasorb 226–09, SKC, Pittsburgh, PA, USA) with a flow rate of 200 mL/min. The flow rate was calibrated using a soap film bubble flow meter prior to and after the shift. Charcoal tubes and diffusive badges were stored at -20°C .

2.4. Pre-treatment and analysis of air samples

Air samples were pre-treated according to methods earlier described (Creta et al., 2017). Briefly, the front and back section of the charcoal tubes were separately extracted with carbon disulfide (purity > 99.9%, Honeywell 342,270, VWR International, Leuven, Belgium). Analysis was performed by gas chromatography with double flame ionization detection (Agilent 7890 B GC). Analysis was simultaneously performed

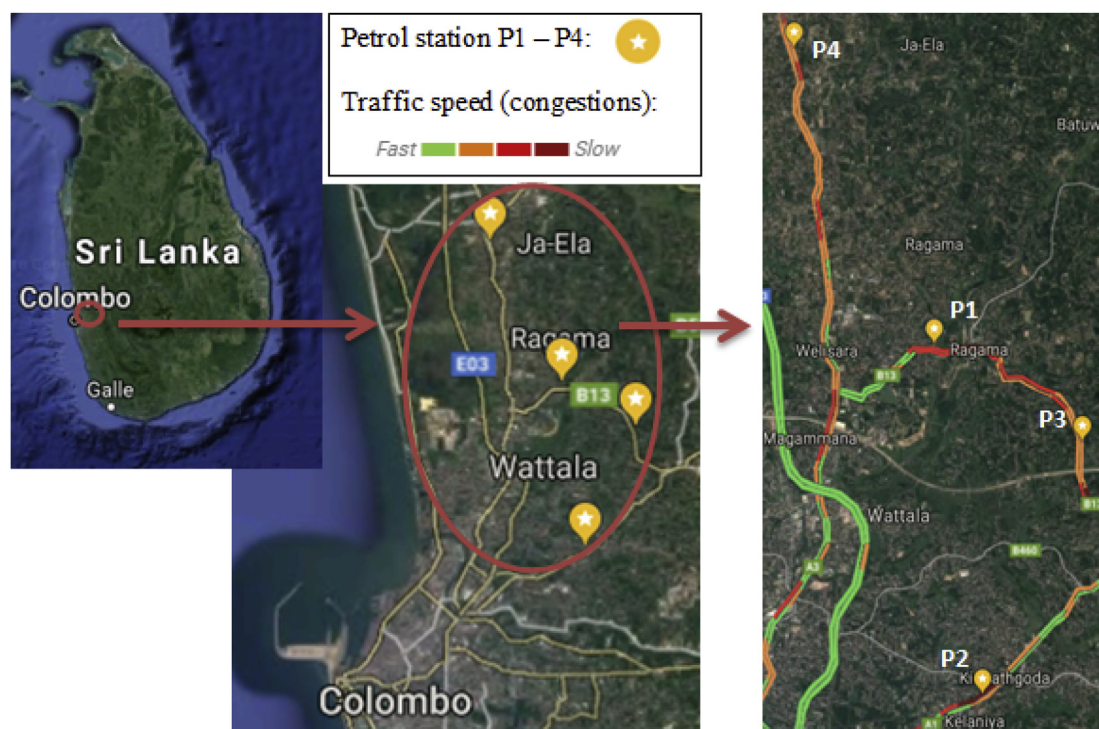


Fig. 1. Western province of Sri Lanka with locations of gas station P1 – P4 and mean traffic speed at the major roads. Gas station P1 is located at Ragama–Mahabage Rd, P2 at Colombo–Kandy Rd, P3 at Kadawatha–Ragama Rd, and P4 at Negombo–Colombo Rd.

on two capillary columns (split-mode) with different polarity, according to an in-house developed and extensively validated method, based on different analytical methods as published by the National Institute for Occupational Safety and Health (NIOSH-methods 1003, 1005, 1019, 1022, 1300, 1301, 1400, 1401, 1402, 1403, 1450, 1454, 1457, 1458, 1459, 1500, 1501, 1552, 1602, 1604, 1609, 1615, 1618, 2500 and 2508). An aliquot of 2 μ L of the sample extract was injected on a SPB-1, 60 m, 0.32 mm i.d., 1.0 μ m film thickness column (apolar) and on a WAX10, 60 m, 0.32 mm i.d., 0.5 μ m film thickness column (polar). Detection by flame ionization was performed at a temperature of 250 °C. Each sample was assayed systematically for the presence or absence of 187 different compounds, including BTX. The different compounds were identified on the basis of a unique set of two relative retention times while quantification was based on a compound-specific relative response factor. An in-house made computer program allowed rapid, automated data-processing of the obtained chromatograms. Upon inter-laboratory comparison tests, the used single-run analytical GC method provided accurate and highly reproducible results of airborne VOC concentrations, with analytical precision generally < 3% and global measurement uncertainty generally < 10%. For the calculation of the air concentration, the compound-specific desorption-efficiency, as well as the measuring time and sample air volume (for charcoal tubes only) were also taken into account. The LOD of the analytical method corresponds to 20 μ g/m³ for an air sample collected over a duration of an 8-h work shift (96 L air volume at 200 mL/min for activated charcoal tube).

2.5. Collection of urine samples

Spot urine samples were collected in plastic bottles with screw caps, before the start of the shift (pre-shift) and after the end of the shift (post-shift). Workers and controls were instructed to provide these samples to researchers who stored these samples in a cool and dark location until transport to the laboratory.

2.6. Pre-treatment and analysis of urine samples

Creatinine was determined using a method based on the Jaffé reaction (Larsen, 1972). S-phenyl mercapturic acid (SPMA, CAS nr 4775-80-8), dichloromethane HPLC grade, ethyl acetate HPLC grade, hydrochloric acid 37% and formic acid LC-MS grade were purchased from Sigma Aldrich. SPMA-d5 (CAS nr 1,331,906-27-4) was purchased from Toronto Research Chemicals. Acetonitrile LC-MS grade and water LC-MS grade came from Biosolve, (Valkenswaard, The Netherlands). Novum SLE cartridges 12 cc were purchased from Phenomenex (Utrecht, The Netherlands).

For calibration and quality control, a stock solution of 1 mg/mL of SPMA was prepared in MeOH/H₂O (1:1 v/v). This solution was diluted with aqua pur to obtain standards in the range of 0.01–10 μ g/mL. For calibration, SPMA was spiked to SPMA-free urine at in the range of 0.05–500 ng/mL. A stock solution of 1 mg/mL for the internal standard SPMA-d5 was prepared and diluted with aqua pur to a working dilution of 10 μ g/mL. Stock solutions, standard solutions and urinary solutions were store at –20 °C. Using this method we could achieve an LOD of 0.05 ng/mL of urine and an LOQ of 0.1 ng/mL of urine.

For sample preparation, urinary solutions and samples were allowed to reach room temperatures. Just over 1 mL of urine was pipetted in a test tube and centrifuged (5 min, at 5400 RPM). From this, 1 mL of the urine was transferred into a new test tube and spiked with 50 μ L of the internal standard (10 μ g/mL) S-PMA-d5 and acidified with 10 μ L of hydrochloric acid (6N) and 940 μ L of aqueous formic acid (1%, pH 7). The mixture was vortexed and purified on a simplified liquid extraction (SLE) column according to manufacturer's instructions. Afterwards, the content of the tube was dried with a nitrogen stream at 40–50 °C. Next, 900 μ L of acetonitrile was added and the tube was vortexed. The solvent was removed using a nitrogen stream at 40–50 °C. This time, 50 μ L water/acetonitrile (80:20) as added as solvent and the vial was vortexed and an aliquot of this solution was injected into the ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) (Xevo TQ-XS Triple Quadrupole Mass Spectrometer (Waters, Zellik, Belgium) for analysis.

For analysis aliquots of 10 μL of samples and standard solutions were injected onto a Kinetex® 1.3 μm C18 100 Å (50 \times 2.1 mm) column, kept at a temperature of 40 °C. Chromatographic separation was achieved, using a mixture of 0.1% of formic acid in water (A) and of 0.1% of formic acid in acetonitrile (B) at a flow rate of 300 $\mu\text{L}/\text{min}$ using the following gradient: from 0 to 0.1 min, 10% of B was held, then increased linearly up to 95% of B from 0.1 min to 2.0 min, hold for 0.6 min and finally, from 2.6 to 3.0 min, the system was allowed to return initial conditions.

2.7. Collection of end-exhaled air samples

End-exhaled air samples were collected by use of a BioVOC sampler (Markes, Llantrisant, UK). Workers were instructed to exhale completely through a cardboard mouthpiece connected to the BioVOC sampler, retaining 140 mL of the alveolar fraction in the sample container (Fig. S1c). This procedure was demonstrated by the researcher just before collection of the sample. Immediately after collection, the sample was transferred to an analytical thermal desorption (ATD) tube. Samples of end-exhaled air were collected before the start of the shift (pre-shift) and at the end of the workday (post-shift) and during three consecutive shifts for gas station attendants and during one shift for office workers. To avoid contamination the samples of gas station attendants were collected in the office of the fuel station or outside on a location upwind from the pump station. Immediately after the sample was collected, the substances of interest were transferred to an ATD tube, which contained Carbograph 1TD and Carbograph 2TD adsorbents (Camsco, Houston, TX, USA). Prior to sampling, all tubes were conditioned in a tube conditioner (TC-20, Markes International, Llantrisant, UK) for 4 h at 250 °C. During conditioning the tubes were purged with helium 5.0 (3,360,150, Linde Gas Benelux, Schiedam, the Netherlands). ATD tubes were capped with brass compression caps and packed in a gastight container and stored and sent by air freight at ambient temperature. Upon arrival the tubes were kept in a gastight container and stored at ambient temperature (Scheepers et al., 2010).

2.8. Analysis of end-exhaled air samples

A BTX calibration standard was used with a stock solution of 2000 ng per μL of methanol (certified reference material, CRM47993, Supelco/Sigma-Aldrich, Zwijndrecht, the Netherlands). Standards were made from this stock solution in methanol (Hipersolv Chromanorm, 20864.320, VWR Chemicals, Amsterdam, the Netherlands) in a range of 0–100 ng/ μL . One μL of each standard was loaded in duplicate on the ATD tubes by use of a loading rig (calibration solution loading rig, C-CSLR, Markes International, Llantrisant, UK). The standards ($N = 8$ in duplicate) and two field blanks were loaded on tubes which were shipped from the Netherlands to Sri Lanka and back to determine if any contamination had occurred during shipment.

The ATD-tubes were analysed using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). This system consists of an autosampler and a thermal desorption unit (Ultra series 2 and Unity series 2, Markes International, Llantrisant, UK) online coupled to a GC-MS (Thermo Focus GC and ISQ MS, ThermoFisher Scientific, Breda, the Netherlands). The first step was to dry purge the tubes in the autosampler. Subsequently, the tubes were desorbed at 250 °C for 15 min. Samples were trapped at -10 °C on a general-purpose hydrophobic trap (U-T2GPH-2S, Markes International, Llantrisant, UK). After desorption at 250 °C, the samples were transferred with helium 5.0 as a carrier gas to a 30 m Rxi-5 MS analytical column (0.25 mm i.d., 0.5 μm film thickness, Restek, Bellefonte PA, USA) with a flow of 1 mL/min. The GC oven was programmed as follows: hold for 1 min at 40 °C; 10 °C/min. to 250 °C. The transfer line and ion source were both kept at 250 °C and the total run time of the samples was 22 min. Full-scan mode with a mass range 35–400 (amu) and dwell time of 0.4 s was used. The data was processed with the Thermo Xcalibur software (Thermo Xcalibur 2.2

SP1.48, Thermo Fischer Scientific). Each tube has a variable background for BTX. Based on 76 blank measurements, the 95% confidence interval was calculated and used as a correction value (upper 95% CI) for the background of the tubes. We were not able to separate m- and p-xylene and therefore have presented the sum of these isomers (as m/p-xylene). Results were expressed in ng/L by adjusting for the Bio-VOC air volume and correspond to an LOD/LOQ of 0.04/0.14 ng/L for benzene, 0.02/0.08 ng/L for toluene, 0.03/0.11 ng/L for m/p-xylene and 0.02/0.08 ng/L for o-xylene.

2.9. Calculations

For samples for which the result of the analysis was below the limit of detection ($< \text{LOD}$) reported by the laboratory, we used half of this LOD for calculations. In gas station attendants, results of PPAS and APAS collected over three shifts were considered to be independent. For all statistical analyses non-parametric tests were used because distributions were skewed. Urinary metabolite concentrations were adjusted for urine density using the creatinine concentrations of each sample. Urine samples with creatinine values below 3 or higher than 30 mmol/L were not included in the analysis. For the results of urine or end-exhaled air analysis we first calculated the average over three work periods, for pre- and post-shift samples, separately.

2.10. Statistical analysis

For population characteristics we used an independent Sample *t*-test for age, Chi-square test for smoker status and a Fisher's Exact test for alcohol use. Differences of BTX concentrations in end-exhaled air and urinary metabolite levels between the pre-shift and post-shift samples were tested using Wilcoxon signed-rank test. The Mann-Whitney *U* test was used to assess differences between gas station attendants and controls for end-exhaled air samples and PPAS/APAS. We calculated post-shift value minus pre-shift values (Δ) for end-exhaled air concentrations. Differences between the four gasoline stations, regarding BTX exposure was then determined with a Kruskal-Wallis test. The contribution of smoking and of sleeping at the gas station was evaluated using a Mann-Whitney *U* test. To evaluate a contribution from exposure to indoor storage road vehicles or fuels a Kruskal-Wallis was used. Correlations between BTX in end-exhaled air, ambient air and between the different methods were assessed by Spearman's rank correlations. A *p*-value < 0.05 was considered as statistically significant. Statistical analyses were performed using SPSS Statistics, version 22 (IBM SPSS Statistics, Vienna, Austria). Compliance with the threshold limit value (TLV) established by the American Conference of Governmental Industrial Hygienists (ACGIH) was tested using IHSTAT (AIHA, 2019).

3. Results

Below the characteristics of the study and the study population are presented. First, the results of BTX air sampling are shown, followed by the results of the analysis of BTX in end-exhaled air and the results of urinary metabolite excretion.

3.1. Study period and environmental conditions

Measurements were conducted in two periods: January 26 – February 26, 2018 and March 14– April 3, 2018. The mean ambient temperature/relative humidity was 25.9 °C/76.0% in the morning (pre-shift) and 30.6 °C/60.8% in the afternoon (post-shift). Wind speed was fairly constant throughout the measurement period and ranged from 3.3 to 7.8 m/s. In January and February, the wind direction was mainly northeast and in March and April the wind was primarily blowing from the southwest (Department of Meteorology, Sri Lanka).

Table 1
Characteristics of the study population.

N	Exposed	Controls	p
	29	16	
Age (y)			0.25 ^a
Mean	39	43	
Minimum	24	24	
Maximum	63	58	
Smoking status (%)			0.27 ^b
Smoker	41	25	
Non-Smoker	59	75	
Alcohol consumption (%)			0.20 ^c
Yes	76	56	
No	24	44	

^a Independent Sample t-test.

^b Chi-square test.

^c Fisher's Exact test.

3.2. Study population

The study populations consisted of 29 males in the exposed group and 16 males in the control group. Table 1 provides some information on the characteristics of the study population.

3.3. Personal air samples

PPAS was performed in all 29 gas station attendants and showed that toluene and benzene were the most abundant with a median (range) of 1370.0 (257–3550) $\mu\text{g}/\text{m}^3$ for toluene and 608.7 (65.1–1960) $\mu\text{g}/\text{m}^3$ for benzene. m-Xylene was observed in only three samples; o-Xylene was only observed in one sample from the worker with the highest exposure to toluene. In the controls BTX was below the LOD in all workers. For workers who participated in APAS, in addition to PPAS, the results are presented in Table 2.

APAS was additionally performed in nine gas station attendants and four control subjects (25% of all measurements). Benzene and toluene were detected in 93% and xylene isomers in 30% of the samples. The concentrations of the xylene isomers were approximately one order of magnitude lower than of benzene and toluene.

Table S1 provides a correlation matrix for the APAS results and shows high correlations between all five BTX components (ranging from $r = 0.774$ to $r = 0.992$). The concentrations of benzene and toluene measured by PPAS were also highly correlated ($r = 0.706$, $p < 0.001$).

In Table S2 the correlations between PPAS and APAS are presented for benzene and toluene. The results of APAS were all correlated with PPAS ($r = 0.677$ – 0.937). Scatter plots of these results are presented in Fig. 2 and Fig. 3 and show that the slope factor of the curve is 0.79 for benzene and 0.92 for toluene, suggesting that PPAS overall resulted in somewhat higher estimates of exposure in the breathing zone compared to APAS.

Table 2

Median (range) of BTX in the breathing zone (in $\mu\text{g}/\text{m}^3$) in gas station attendants. Selection of workers who participated in both APAS and PPAS.

Substance	N ^a	Active personal air sampling (APAS)	N ^a	Passive personal air sampling (PPAS) ^b
Benzene	25	225 (32.3–1300)	25	392 (65.1–1960)
Toluene	25	445 (54.4–3110)	25	745.6 (< 5.0–2770)
o-Xylene	25	43.3 (< 20.0–225)	25	< 20.0
p-Xylene	25	25.1 (< 20.0–181)	25	< 20.0
m-Xylene	25	75.9 (< 20.0–411)	25	< 20.0

^a Non-detects were included as LOD/2.

^b The median (range) of the PPAS is based on a selection of the measurements of workers who also participated in APAS.

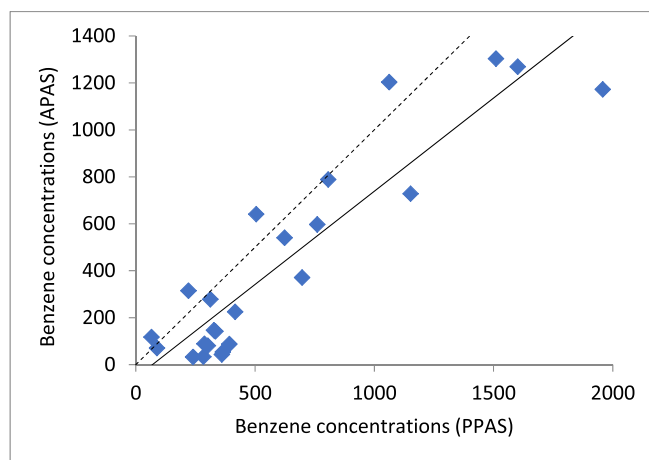


Fig. 2. Correlation between PPAS and APAS for benzene in $\mu\text{g}/\text{m}^3$. The Spearman's rank correlation is 0.804. The dotted line unity ($x = y$). The slope factor is 0.79.

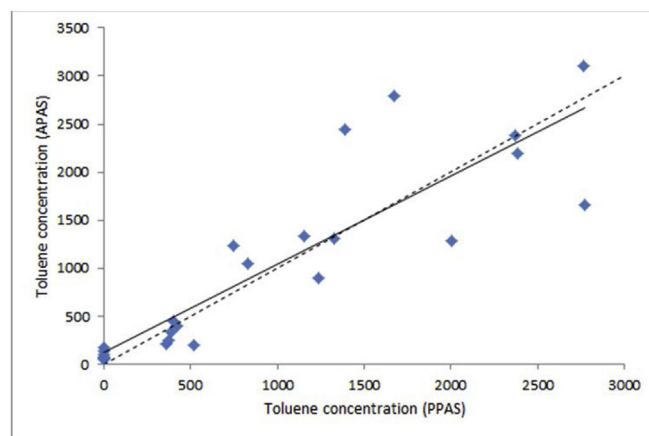


Fig. 3. Correlation between PPAS and APAS for toluene in $\mu\text{g}/\text{m}^3$. The Spearman's rank correlation coefficient is 0.935. The dotted line unity ($x = y$). The slope factor is 0.92.

The results of the VIDITA analysis are presented in Table 3 and Fig. 4. During refilling of road vehicles, the concentrations were in the low ppm range and occurred in spikes of exposure in the breathing zone (with a maximum of 2.24 ppm). Much higher concentrations of fuel vapours were detected when opening the fuel storage tank to determine the fuel level in the main fuel storage tank of the petrol station. After a gradual increase a maximum concentration of 96.4 ppm was reached in the breathing zone of the worker.

The gas station attendant used a metal measuring rod to determine the fuel level and then wiped off the fuel residue using a cleaning towel. The third task leading to high exposure was related to refilling of the pump station main storage tank. Opening of the tank and connecting the hose from the tanker truck resulted in the highest peak recorded, corresponding to a maximum of 239 ppm. No personal protective equipment was used when conducting these tasks.

3.4. End-exhaled air

In Table 4 an overview is provided of all end-exhaled air concentrations observed in pre- and post-shift samples for gas station attendants as well as controls. All substances of interest were detected in exhaled air of both workers and controls. The change from pre-shift to post-shift in the gas station attendants indicates that the work environment resulted in a build-up of BTX in the body followed by

Table 3

Tasks with peak concentrations in ppm (see Fig. 4 for the corresponding video images).

Task	Description	Recording time (sec)	Peak concentration (ppm)
Refill of customer tank	Refilling of tank of road vehicles with petrol. The nozzle is at a distance of approximately 0.5 m from the breathing zone.	25	2.24
Measurement of fuel level in storage tank	Checking gasoline level in the main gasoline storage tank. The storage tank is opened and the measuring rod is used to determine the fuel and is then cleaned with a towel.	45	96.4
Refill of main fuel storage tank	The gas station attendant opens the main gasoline storage tank of the petrol station. The truck driver connects a hose and starts the refill process.	60	239

Table 4

Median (range) concentrations of BTX in end-exhaled air in ng/L.

Substance	Sample	Exposed (N = 29)	p ^b	Control (N = 16)	p ^b	p ^c
Benzene	Pre-shift	10.8 (7.07–49.6)	< 0.0001	9.47 (6.11–19.2)	0.121	0.003
	Post-shift	20.6 (6.99–88.3)		10.9 (7.74–20.5)		
	Δ ^a	7.38 (–17.3–79.6)		1.46 (–8.79–9.27)		
Toluene	Pre-shift	10.3 (4.18–205)	0.002	3.09 (1.39–14.0)	0.326	0.001
	Post-shift	22.7 (5.96–126)		3.91 (1.72–9.47)		
	Δ ^a	11.4 (–105–111)		0.68 (–7.75–4.88)		
m/p-Xylene	Pre-shift	1.59 (0.66–48.9)	0.003	0.69 (0.21–1.34)	0.569	0.002
	Post-shift	2.33 (0.71–23.4)		0.70 (0.41–1.49)		
	Δ ^a	0.79 (–35.1–21.6)		–0.06 (–0.29–0.90)		
o-Xylene	Pre-shift	1.34 (0.57–39.6)	0.003	1.22 (0.53–1.71)	0.023	0.308
	Post-shift	2.40 (0.90–14.7)		1.43 (0.75–5.09)		
	Δ ^a	0.71 (–29.6–13.5)		0.59 (–0.51–3.86)		

^a Post-shift value minus pre-shift value.^b Pre-shift vs. post-shift values in Mann-Whitney *U* test.^c Gas station attendants vs. controls in Mann-Whitney *U* test.

elimination via the airways. For toluene the median post-shift concentrations were the highest (fivefold the values observed in controls) as well as the increase over the shift compared to controls (fifteen times higher than in controls).

For benzene the end-exhaled air concentrations observed in gas station attendants were twofold those observed for controls at the start of the shift and a fivefold increase from pre-to post-shift was observed for gas station attendants compared to controls. For toluene and xylene, the pre-shift values in gas station attendants were elevated compared to pre-shift values in the office workers. The concentrations of the xylene isomers were one order of magnitude lower than for benzene and toluene. Xylene concentrations in exposed and control subjects were similar. In controls a statistically significant increase was observed for o-xylene from pre-shift to post-shift ($p = 0.023$). Table S3 shows a correlation table for all components of interest. Benzene and toluene and toluene were strongly correlated with m/p-xylene and o-xylene ($r = 0.727$ – 0.829). The correlations between benzene and xylene-isomers were moderate ($r = 0.525$ – 0.611).

On the day that 19 workers reported to have had direct skin contact due to a spill the post shift values for BTX and the increase from pre-shift to post-shift was significantly higher compared to the end-exhaled concentrations in 10 workers who had reported not to have direct contact with fuels. The effect was observed for all compounds of interest except for o-xylene (Table 5). On two other days direct skin contact due to a self-reported spill did not result in an increase.

In Fig. 5 the end-exhaled concentrations are arranged by smoking status for both gas station attendants and office workers, separately. In both groups the influence of smoking was most pronounced in the pre-shift samples (see Table S4 for the corresponding p-values). For benzene this was the only statistically significant change ($p < 0.01$). For toluene and o-xylene the change from pre-shift to post shift was threefold to fourfold higher in gas station attendants ($p < 0.005$) but no difference was observed in office workers. These differences between smokers and non-smokers were much weaker and not statistically significant for benzene and m/p-xylene. Non-smoking gas station

attendants numbers 7, 12 and 17 have extremely high values for multiple components that may be explained by a common source (fuel or vehicle exhaust). For other extreme values in both smokers and non-smokers (9, 18, 27, 31, 45) no pattern was observed across components of the BTX mixture and we were not able to explain these values.

In office workers the effect of smoking should be interpreted with caution because of the small number of smokers ($n = 4$). In this group the effect of smoking was also the most pronounced on toluene and xylenes. For toluene and o-xylene the pre-shift value in smokers was 1.5 to 2-fold higher than in non-smokers. The end-exhaled concentrations for toluene and m/p-xylene were higher at the end of the shift but for none of the substances the change from pre-shift to post-shift was increased.

The results of the analysis of SPMA in urine samples are presented in Table 6. In addition to the results for the workers and controls, we presented the results disaggregated by current smoking status. Urinary SPMA levels over a wide range were observed. For the total group of gas station attendants, the pre-shift values were higher compared to the values observed in office workers. The increase from pre-shift to post shift was 3 to 4-fold higher in the gas station attendants compared to the controls. The contribution from smoking was small, except for the pre-shift value in the smokers among office workers. This pre-shift value was somewhat higher compared to non-smokers (2.58 vs. 0.36 $\mu\text{g/g}$) but because of the small number of four smokers these results should be interpreted with caution. None of the comparisons for smoking status indicated a statistically significant difference. For the non-smokers we did not observe a difference in post-shift values by exposure group.

4. Discussion

In this study we collected personal samples to compare the BTX exposure in gasoline attendants with office workers. Below the results of the air sampling will be discussed in more detail, followed by an evaluation of the biomonitoring outcomes.

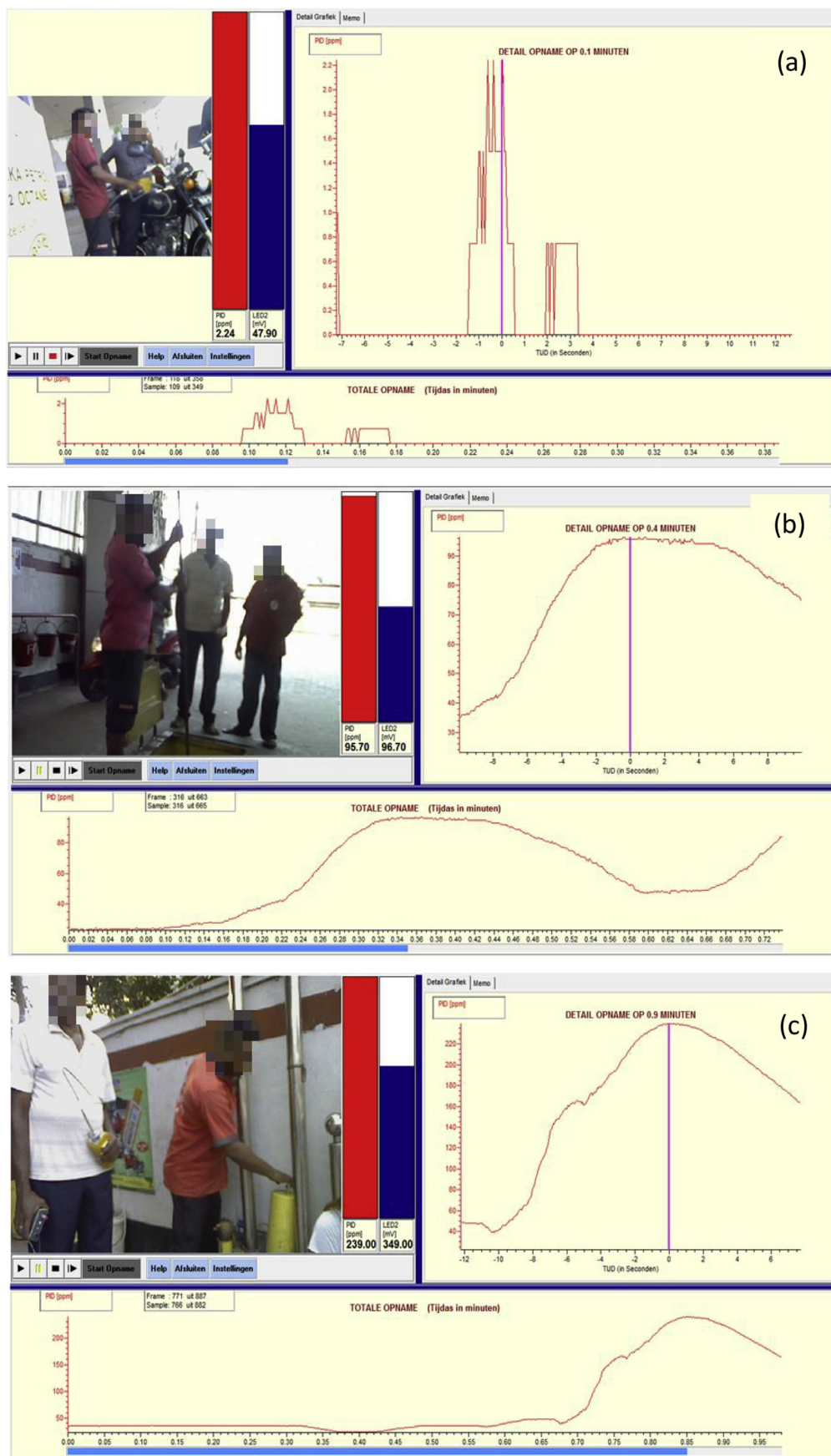


Fig. 4. Examples of VIDITA recordings for three tasks (see Table 4 for details). The real-time VOC concentration (ppm) is indicated by the red bar next to the video image. The upper large graph shows the exposure-time pattern of the PID signal in seconds. On the lower smaller panel, the exposure-time is shown in minutes. The purple vertical line in the upper panel corresponds to the time (also indicated by the blue bar under the small panel). The following tasks are presented: Refill of customer tank (a), measurement of fuel level in storage tank (b) Refill of main fuel storage tank (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 5

Median (range) of BTX concentrations in end-exhaled air by skin exposure in ng/L.

Day	Substance	Time of sample	Skin exposure (N = 24)	No skin exposure (N = 5)	p ^a
Day-1	Benzene	Post-shift	18.3 (8.38–124)	21.4 (9.18–23.5)	0.674
		Δ^a	8.92 (–7.25–116) ^b	10.4 (–26.7–13.8)	0.600
	Toluene	Post-shift	15.4 (6.30–178)	25.7 (8.50–44.5)	0.933
		Δ^a	9.76 (–13.2–140) ^b	19.6 (–22.73–32.2)	0.908
	m/p-Xylene	Post-shift	2.07 (0.65–25.2)	1.98 (1.12–2.32)	0.758
		Δ^a	0.33 (–1.66–19.9) ^b	0.53 (–1.35–1.27)	1.000
Day-2	Benzene	Post-shift	1.87 (0.63–19.5)	2.42 (0.68–3.55)	0.933
		Δ^a	0.36 (–2.72–16.0) ^b	1.18 (–0.85–1.61)	0.413
	Toluene	Post-shift	23.1 (5.24–106)	8.88 (2.84–71.2)	< 0.01
		Δ^a	13.3 (–45.9–96.4)	–1.02 (–55–61.7)	< 0.05
	m/p-Xylene	Post-shift	37.1 (3.77–358)	7.49 (2.62–128)	< 0.05
		Δ^a	16.9 (–57.8–3412)	–2.74 (–323–114)	0.056
Day-3	Benzene	Post-shift	3.65 (0.49–65.8)	1.30 (0.31–12.20)	< 0.05
		Δ^a	1.23 (–5.67–63.4)	–0.04 (–48.22–10.2)	0.126
	Toluene	Post-shift	2.51 (0.76–41.9)	1.20 (0.55–8.48)	0.085
		Δ^a	1.59 (–2.76–40.2)	–0.03 (–62.5–7.08)	0.104
	m/p-Xylene	Post-shift	9.47 (4.68–117)	9.48 (5.86–22.5)	0.549
		Δ^a	6.05 (–110.27–29.8)	9.39 (–2.41–17.7)	0.324
Day-3	Toluene	Post-shift	9.80 (2.64–565)	8.35 (2.62–37.1)	0.793
		Δ^a	7.70 (–545–46.7)	12.8 (–12.1–38.9)	0.518
	m/p-Xylene	Post-shift	1.37 (0.49–139)	1.03 (0.30–5.65)	0.324
		Δ^a	0.89 (–15.3–3.74)	0.50 (–1.80–5.12)	0.867
	o-Xylene	Post-shift	0.94 (0.30–114)	1.56 (0.66–4.20)	0.114
		Δ^a	0.31 (–112–2.92)	0.67 (–2.73–5.90)	0.487

² Comparison between skin exposure and no skin exposure for post-shift and Δ (post - pre) with the Mann-Whitney U test.^a Δ Post-shift value minus pre-shift value.^b N = 23.

4.1. Personal air sampling

Personal measurements collected in the breathing zone indicated that gas station attendants have an enhanced exposure to BTX compared to office workers. High correlations between the components of interest were reported and indicate a common source i.e. fossil fuels and incomplete combustion from road vehicle exhaust emissions (IARC, 2014).

The PPAS measurements were less sensitive than APAS and not all xylene isomers could be detected. PPAS correlated reasonably well with APAS but on average overestimated APAS outcome for benzene by 26% and for toluene by 10%. Passive and active air sampling normally lead to corresponding results (Harper, 2000) but our study indicates that the mean deviation for benzene is considerable.

Smoking had a small but significant influence on the benzene values in the breathing zone samples and for toluene this influence was of borderline statistical significance ($p = 0.074$). As smoking was prohibited during work hours this difference may be explained by smokers exhaling higher levels of benzene and toluene in their breathing zones compared to non-smokers. This contribution of exhaled VOC as an interference of personal air samples was not reported before. This phenomenon should be further studied as it may influence the results of personal air sampling (Ras et al., 2009).

Of all PPAS, two measurements exceeded the threshold limit value (TLV) of 1.6 mg/m³ for benzene exposure (of the American Conference of Governmental Industrial Hygienists, ACGIH) and approximately 30% of the measurements exceeded half of the TLV. The probability for an individual worker to exceed the TLV was calculated to be 3.4%. When taking into account long working hours by adjustment of the exposure to time-weighted average of 8-h, the number of measurements exceeding the TLV was 28 (Fig. S3). In total for 14 workers of P2, P3 and P4 the measured exposure was above the current TLV. After adjustment to an 8-h shift the probability of exceeding the TLV was calculated to be 27%.

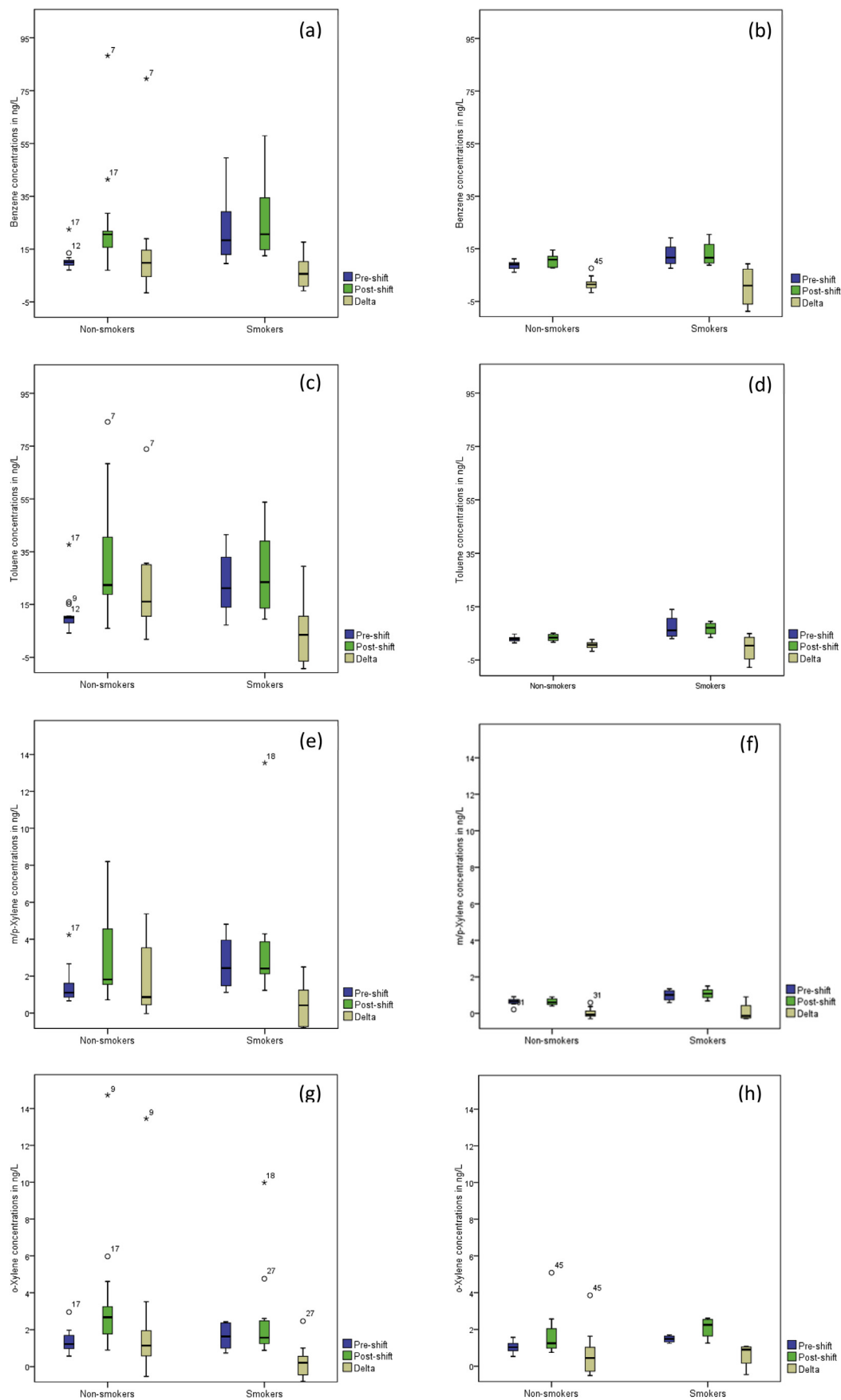
Three different tasks were analysed by comparison of the video images with the real-time recording of the fuel vapours using the VIDITA system (Fig. S1). Because of the PID monitor used for real-time

measurements it was not possible to measure specific components or calibrate the read-out to mg/m³ units. Nevertheless, this set-up allowed to analyse tasks and engage the workers to participate in finding ways to further reduce task-based peak exposures. The highest peaks recorded were related to measurement of the fuel level and refilling of the main fuel storage tank. Similar as in the refilling of small tanks in road vehicles, adding fuel to an empty tank will cause a large volume of saturated vapor to stream out of the tank opening, close to the breathing zone of the worker who is involved in performing this task. In addition to inhalation exposure, the video recordings showed that direct skin contact with fuel occurred (Alves et al., 2017).

Ghittori et al. (2005) studied 26 gas station attendants in Pavia, Lombardia, Italy and found much lower average (\pm sd) benzene concentrations of 38.81 \pm 24.26 μ g/m³, ranging from 1.71 to 178.28 μ g/m³. In a study of gas station attendants in five service stations in Taegu, Republic of Korea, Jo and Song (2001) observed 4 to 5-fold lower pre-shift benzene levels of 84.4 \pm 33.2 and in smokers and 72.1 \pm 16.0 μ g/m³ in non-smokers. For toluene these levels were 5 to 10-fold lower 141 \pm 18.2 and 126 \pm 42.0 μ g/m³, respectively. The xylene isomers were 2- to 3-fold lower, ranging from 13.1 to 24.0 μ g/m³ in non-smokers to 13.0–26.5 μ g/m³ in smokers. The work hours were limited to 6–8 h per day. Such differences could be explained by the type of fuel dispense technology used (with or without fume extraction), the composition of fuels regarding BTX content, environmental conditions such as temperature and wind speed as well as the intensity and the type of emissions from e.g. passing road traffic (use of three-way catalysers for gasoline powered vehicles) (Masih et al., 2018).

4.2. End-exhaled air

The measurement of end-exhaled air provided us with an integrated exposure estimate for BTX. It reflects mainly recent inhalation exposure but will also indicate potential additional uptake from other routes such as skin absorption at work and co-exposures from traffic and specific sources at home. Earlier studies showed that a morning sample may reflect exposure of the previous day and also reflects a history of exposure due to retention of BTX (Chen et al., 2002; Pellizzari et al., 1992;



(caption on next page)

Fig. 5. End-exhaled air concentrations in ng/L arranged smoking status for benzene (a, b), toluene (c, d), m/p-xylene (e, f) and o-xylene (g, h). Left panels (a, c, e and g) show the results in gas station attendants; right panels show the controls (b, d, f and h). For the p-values see Table S4. In gas attendants seven of the results for toluene are off-scale: one median pre-shift value in a non-smoker of 126 ng/L and three values in smokers: 128 and 205 ng/L in pre-shift values and one post-shift value of 109 ng/L. In addition three deltas were not shown: -97 and -105 for smokers and +111 for a non-smoker. The boxplots show median, 1st and 3rd quartiles and the whiskers show the range. Extremes are indicated by symbols and accompanying participant numbers.

Scheepers et al., 2010; Marchand et al., 2015). Earlier exhaled air monitoring in the field of refuelling suggested that environmental determinants rather than individual factors are driving exhaled air levels of BTX (Egeghy et al., 2000; Egeghy et al., 2002).

Our observed mean pre-shift benzene concentration of 10.8 ng/L in workers and 9.47 ng/L in controls (Table 5) corresponds well with earlier reports of 8.6 ng/L in a study of self-service refuelling in the US (Egeghy et al., 2002) and likely reflects exposures during commuting to work (Ballesta et al., 2006; Weisel et al., 1992, 2010). In gas station workers we observed an almost two-fold increase of the median concentration in pre-shift to post-shift ($p < 0.005$) that was not observed in the control group (except for o-xylene where an increase in the median exhaled air was observed from 1.22 to 1.43 ng/L, $p = 0.023$). There are three explanations for higher pre-shift values in gas station attendants compared to controls: most workers had been exposed the previous day(s) and the excretion from adipose tissue will add to the pre-shift concentration of the next day(s) (Hajimiragha et al., 1989; Pellizzari et al., 1992). Second, some workers had been sleeping overnight at the petrol station locations which may have resulted in an elevated background exposure compared to office workers. The effect of sleeping location (Table S6) was observed for benzene and m/p-xylene ($p < 0.05$) and toluene ($p = 0.08$) but only in the post-shift sample and in the change from pre-shift to post shift (benzene and m/p-xylene) but not in the first sample collected in the morning before the start of the shift. This lag could be explained by the somewhat slower kinetics due to the low physical activity during sleep followed by enhanced excretion related to the much higher physical activity level during work hours. The third factor that could contribute to explain this difference is the contribution of smoking that was more frequent among gas station attendants compared to office workers (Table 1). The contribution from smoking will be further discussed below.

The within person change from pre-to post-shift indicates a similar pattern of clearly enhanced exposure at the petrol station work location for all substances in the BTX mixture (Table 4). This change was not observed in office workers who served as controls, except for o-xylene where the control persons showed an increase over the work shift with a median of 0.59 ng/L that came very close to the increase by 0.71 ng/L of the gas station attendants. This suggests that there may have been a work-related exposure to o-xylene (but not to m/p-xylene) for control persons. The most likely origin is that of traffic close to the hospital buildings that are found at the university campus where the control persons were working. An alternative explanation may be related to background exposure from exposure during commuting or from the home environment which may be different between gas station workers

and gas station attendants e.g. due to social-economic factors.

Despite the differences in work hours, the shift rotation system and off-work exposure duration and frequency between petrol stations, we did not observe statistically significant differences in BTX in end-exhaled air depending on the petrol station (Table S8) with the exception of the concentration of 5.18 ng/L of m/p-xylene that was higher in P3 ($p < 0.01$) compared to the other three petrol stations (2.13 ng/L in P1, 2.42 ng/L in P2 and 1.35 ng/L in P4). P3 and P4 were the stations with the long working hours (up to 15 h/day) with only one or two days off-work per month.

Smoking had a profound influence on the benzene content in end-exhaled air samples (Hajimiragha et al., 1989; Lin et al., 2008). The within-person change from pre-shift to post-shift indicated a remarkable two-fold increase in non-smokers compared to smokers in toluene and o-xylene ($p < 0.02$). For benzene and m/p-xylene this difference was of only borderline significance ($p = 0.13$ for benzene and $p = 0.09$ for m/p-xylene).

In the pre-shift samples the smokers had a two-fold higher exposure for all components which was statistically significant for benzene, toluene and m/p-xylene ($p < 0.01$) but not for o-xylene ($p = 0.21$). These differences may be explained by smoking in the morning prior to providing the pre-shift sample. It is useful to determine the change from pre-shift to post-shift as a proxy of work-related exposure. The gas stations enforced a very strict no-smoking policy because of the high flammability of the fuels handled. Because of that the influence of smoking that was seen in the pre-shift sample was not observed in the post-shift. In smokers the changes from pre- to post-shift were four-fold for toluene ($p < 0.01$), three-fold for o-xylene ($p < 0.05$) but only two-fold and not statistically significant for both benzene ($p = 0.13$) and m/p-xylene ($p = 0.37$).

In addition to working as a gas station attendant and smoking as important determinants of exposure to BTX, we studied some other factors that could lead to co-exposure. Thirteen workers stayed overnight at the gas station because they lived far away from work. This group was compared to a group of sixteen workers who went home after work. Between these groups no differences were observed in pre-shift BTX concentrations but for benzene and m/p-xylene post-shift and the change from pre-to post-shift showed an increase ($P < 0.05$) that was larger in the workers who slept-over at work compared to those who went home after work (Table S6).

A condition that has been implicated to influence BTX exposure is having a garage with a direct connection to the home, which would allow fuel and exhaust emissions to penetrate to the living part of the home (Thomas et al., 1993; Adgate et al., 2004; Scheepers et al., 2010).

Table 6

Median and range of urinary excretion of SPMA in $\mu\text{g/g}$ creatinine.

Group	Timing	Total	Smoker	Non-Smoker	p^b
		N = 29	N = 12	N = 17	
Gas station attendants	Pre-shift	2.40 (0.08–7.77)	2.31 (0.66–7.14)	2.58 (0.08–7.77)	0.98
	Post-shift	3.02 (0.12–15.5)	3.36 (0.62–8.31)	2.24 (0.12–15.5)	0.50
	Δ^a	0.58 (–2.07–12.9)	0.87 (–1.35–3.98)	0.41 (–2.07–12.9)	0.55
		N = 16	N = 4	N = 12	
Office workers	Pre-shift	0.55 (< 0.01–10.9)	1.38 (0.23–2.68)	0.36 (< 0.01–10.9)	0.25
	Post-shift	1.07 (< 0.01–14.7)	1.07 (1.07–10.7)	2.64 (< 0.01–14.7)	0.63
	Δ^a	0.16 (–2.57–11.1)	–0.31 (–0.40–9.45)	2.11 (–2.57–11.1)	0.47

^a Post-shift value minus pre-shift value.

^b Comparison of smokers and non-smokers in Mann Whitney U test.

In this study, we did not observe an influence of keeping a fuel or fuel-powered vehicle in a garage with a direct open-air connection to the living quarters of the residence (Table S7). We also did not observe any differences between the four gas stations, regarding the BTX content in exhaled air, pre-shift, post-shift or change over the work period (Table S7).

Some of the workers reported to have encountered a situation with direct contact such as a spill of fuel on the skin or on the clothes. As these events were reported on a day-to-day basis with a high frequency (24 for day-1, 19 for day-2 and 21 for day-3) we could compare the frequency of reported spills in post-shift end-exhaled air concentrations and also to the change from pre-shift to post-shift. Spills were associated with an increase of benzene (2–3 fold), toluene (5-fold) and m/p-xylene (3-fold). The increase was statistically significant for all of these comparisons (Table 5) and could be the result of inhalation from contaminated clothes as well as dermal absorption as a result of direct skin contact (Fent et al., 2015). However, similar reports on two other days did not result in an increased exhalation of BTX. Therefore, this finding only provides limited evidence for an increased dermal uptake due to skin contamination.

In the study of gas station attendants in five service stations in Taegu, Republic of Korea Jo and Song (2001) observed 2–4-fold higher pre-shift benzene levels of 26.6 ± 14.5 and benzene post-shift values of 41.0 ± 14.7 ng/L. For toluene these levels were 40.2 ± 17.5 and 63.6 ± 18.8 $\mu\text{g}/\text{m}^3$, respectively. The xylene isomers were also 2–4-fold higher. The work hours were limited to 6–8 h per day. Because the personal air samples indicated much lower inhalation exposure and the end-exhaled air sample higher values there may have been another source of exposure. As the data reported by Jo and Song were stratified for smoking this can be ruled out as an explanation. Other factors may have caused this mismatch, e.g. a high contribution of dermal absorption, but this factor was not discussed by the authors.

4.3. Urinary SPMA

The median level of excretion of urinary SPMA in the pre-shift urine was 4-fold higher in gas station workers compared to office workers (2.40 vs. 0.55 $\mu\text{g}/\text{g}$). The long-working hours (and resulting few hours off-work to recuperate) may have contributed to accumulation of the benzene body burden over the workweek (Carrieri et al., 2019). This is in line with the estimated half-life of excretion in humans of 9.0 ± 2.4 h (Boogaard and van Sittert, 1995). The post-shift values were similar and suggest that there was a substantial background of benzene that contributed to urinary SPMA excretion (Lovreglio et al., 2010). In smokers the results of urinary SPMA were consistent with end-exhaled analysis of benzene with very similar findings in smokers indicating no change from pre-shift to post-shift. In non-smokers the results median SPMA excretion from pre-shift to post-shift were somewhat inconsistent with the median end-exhaled benzene levels that indicated a two-fold increase. Overall the entire range of SPMA values remained well below 50% of the biological exposure index (BEI) of 25 $\mu\text{g}/\text{g}$ (ACGIH). This level of urinary SPMA excretion does not support a pronounced contribution from dermal absorption, as this would not be in line the estimate of inhalation exposure by personal air sampling that indicated exceedance of the occupational exposure level. In the Italian gas station workers Ghittori et al. (2005) reported very similar average (\pm sd) SPMA values of 2.36 ± 1.82 $\mu\text{g}/\text{g}$.

5. Conclusion

This study showed that gas station attendants have an elevated inhalation exposure to BTX compared to office workers. This was observed by personal air sampling in the breathing zone, in end-exhaled air and also by analysis of urine samples. For one out of four participating gas station attendant's inhalation exposure to benzene was above the current TLV for an 8-h shift but this was not reflected to that extent

in the urinary excretion of SPMA (that did not exceed the TLV-equivalent BEI). Elevated pre-shift values of benzene in exhaled air indicated accumulation of work-related benzene exposure over time. In addition, some tasks with short-term exposures were identified. For the benzene biomarkers smoking was identified as a contributing co-exposure but other sources of ambient exposure could not be confirmed as significant sources of co-exposure for benzene and the other substances of interest. A reduction of the long working hours offering workers to recuperate during regular periods of no-exposure is considered the most effective way to reduce exposure. Second, from exhaled air we found indications to suggest that workers who slept at the gas station were higher exposed than those who recuperated at home. It is expected that the body burden for benzene as reflected in enhanced pre-shift exhaled air could be reduced by extending the no-exposure recuperation period between two shifts to 16 h per day. Sharing these occupational hygiene analyses with the workers and their employer may lead to engagement of workers and involve them in mitigating measures that may further reduce both exposure concentrations and duration and the introduction of personal protective equipment to avoid peaks of inhalation and dermal exposures.

Acknowledgment

This project is a part of the EU-Cost Action, CA 15129 (DiMoPEX). The Cost action is supported by the EU Framework Program Horizon 2020. The study was supported with the Foreign Award 2017 of the Dutch Occupational Hygiene Society (NVvA) and by funding the University of Kelaniya research grant RP/03/04/03/01/2017. The authors thank Henny Giesbers, Gert van Voorst and Stef Mientki for their role in the design and development of VIDITA hardware and software. The authors are grateful Ms. Tharuka Dissanayaka and Ms. Imalka Weerasooriya for their support of the field work. Ms. Katrien Poels is acknowledged for her contribution to the instrumental analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2019.108670>.

References

- Adgate, J.L., Eberly, L.E., Stroebe, C., Pellizzari, E.D., Sexton, K., 2004. Personal, indoor and outdoor VOC exposures in a probability sample of children. *J. Expo. Anal. Environ. Epidemiol.* 14, S4–S13.
- Alves, L.P., Vieira, D.S., Nunes, L.S.S., Cruz, L.P., Reis, A.C.S., Gomes, Í.V., Luz, S.R., Santos, A.V.S., Esteves, M.B., 2017. Relationship between symptoms, use of PPE and habits related to occupational exposure to BTEX compounds in workers of gas stations in Bahia, Brazil. *J. Environ. Prot.* 8 (05), 650.
- Amorim, L.C.A., Cardeal, Z.L., 2007. Breath air analysis and its use as a biomarker in biological monitoring of occupational and environmental exposure to chemical agents. *J. Chromatogr. B* 853 (1–2), 1–9.
- Ballesta, P.P., Field, R.A., Connolly, R., Cao, N., Caracena, A.B., De Saeger, E., 2006. Population exposure to benzene: One day cross-sections in six European cities. *Atmos. Environ.* 40 (18), 3355–3366.
- Boogaard, P.J., van Sittert, N.J., 1995. Biological monitoring of exposure to benzene: a comparison between S-phenylmercapturic acid, trans,trans-muconic acid, and phenol. *Occup. Environ. Med.* 52 (9), 611–620.
- Carrieri, M., Pignini, D., Martinelli, A., Paci, E., Maratini, F., Salamon, F., Tranfo, G., 2019. Effect of benzene exposure on the urinary biomarkers of nucleic acid oxidation in two cohorts of gasoline pump attendants. *Int. J. Environ. Res. Public Health* 16 (1) Jan 5.
- Caro, J., Gallego, M., 2009. Environmental and biological monitoring of volatile organic compounds in the workplace. *Chemosphere* 77 (3), 426–433.
- Chen, M.-L., Chen, S.-H., Guo, B.-R., Mao, I.-F., 2002. Relationship between environmental exposure to toluene, xylene and ethylbenzene and the expired breath concentrations for gasoline service workers. *J. Environ. Monit.* 4 (4), 562–566.
- Creta, M., Poels, K., Thoenen, L., Vranckx, K., Collaerts, P., Jansen, F., Vangeel, M., Godderis, L., Duca, R.-C., Vanoirbeek, J.A.J., 2017. A method to quantitatively assess dermal exposure to volatile organic compounds. *Ann. Work Expo. Health* 61, 975–985.
- De Oliveira, K., Martins, E., Arbilla, G., Gatti, L., 2007. Exposure to volatile organic compounds in an ethanol and gasoline service station. *Bull. Environ. Contam. Toxicol.* 79 (2), 237–241.
- Edokpolo, B., Yu, Q.J., Connell, D., 2014. Health risk assessment of ambient air

- concentrations of benzene, toluene and xylene (BTX) in service station environments. *Int. J. Environ. Res. Public Health* 11 (6), 6354–6374 Jun 18.
- Egeghi, P.P., Tornero-Velez, R., Rappaport, S.M., 2000. Environmental and biological monitoring of benzene during self-service automobile refueling. *Environ Health Perspect* 108 (12), 1195–1202.
- Egeghi, P.P., Nylander-French, L., Gwin, K.K., Hertz-Picciotto, I., Rappaport, S.M., 2002. Self-collected breath sampling for monitoring low-level benzene exposures among automobile mechanic. *Ann Occup Hyg* 46 (5), 489–500.
- Fent, K.W., Evans, D.E., Booher, D., Pleil, J.D., Stiegel, M.A., Horn, G.P., Dalton, J., 2015. Volatile organic compounds off-gassing from firefighters' personal protective equipment ensembles after use. *J. Occup. Environ. Hyg.* 12 (6), 404–414.
- Ghittori, S., Ferrari, M., Maestri, L., Negri, S., Zadra, P., Gremida, C., Imbriani, M., 2005. The significance of environmental and biological monitoring in workers employed in service stations after the elimination of tetraethyl lead from gasoline. *G. Ital. Med. Lav. Ergon.* (2), 137–153 Apr–27.
- Gross, S.A., Paustenbach, D.J., 2018. Shanghai Health Study (2001–2009): what was learned about benzene health effects? *Crit. Rev. Toxicol.* 48 (3), 217–251 Mar.
- Hajimiragha, H., Ewers, U., Brockhaus, A., Boettger, A., 1989. Levels of benzene and other volatile aromatic compounds in the blood of non-smokers and smokers. *Int. Arch. Occup. Environ. Health* 61 (8), 513–518.
- Harper, M., 2000. Sorbent trapping of volatile organic compounds from air. *J. Chromatogr. A* 885 (1–2), 129–151.
- Hulke, S.M., Patil, P.M., Thakare, A.E., Vaidya, Y.P., 2012. Lung function test in petrol pump workers. *Natl. J. Physiol. Pharm. Pharmacol.* 2 (1), 71–75.
- IARC, 2014. Diesel and Gasoline Engine Exhausts and Some Nitroarenes. IARC Monograph on the Evaluation of Carcinogenic Risks to Humans, vol. 105 IARC, Lyon, France.
- Jo, W.K., Song, K.B., 2001. Exposure to volatile organic compounds for individuals with occupations associated with potential exposure to motor vehicle exhaust and/or gasoline vapor emissions. *Sci. Total Environ.* 269 (1–3), 25–37.
- Kitwattananavong, M., Prueksasit, T., Morknoy, D., Tunsaringkarn, T., Siri Wong, W., 2013. Health risk assessment of petrol station workers in the inner city of Bangkok, Thailand, to the exposure to BTEX and carbonyl compounds by inhalation. *Hum. Ecol. Risk Assess. Int. J.* 19 (6), 1424–1439.
- Kulathunga, D.R., Mahanama, K.R.R., 2013. Fingerprinting diesel and petrol fuels for adulteration in Sri Lanka. *J. Nat. Sci. Found. Sri Lanka* 41 (4), 287–292 2013.
- Larsen, K., 1972. Creatinine assay by a reaction-kinetic principle. *Clin. Chim. Acta* 41, 209–217.
- Lin, Y.S., Egeghi, P.P., Rappaport, S.M., 2008. Relationships between levels of volatile organic compounds in air and blood from the general population. *J. Expo Sci Environ Epidemiol* 18 (4), 421–429.
- Lovreglio, P., Barbieri, A., Carrieri, M., Sabatini, L., Fracasso, M.E., Doria, D., Drago, I., Basso, A., D'Errico, M.N., Bartolucci, G.B., Violante, F.S., Soleo, L., 2010. Validity of new biomarkers of internal dose for use in the biological monitoring of occupational and environmental exposure to low concentrations of benzene and toluene. *Int. Arch. Occup. Environ. Health* 83 (3), 341–356 Mar.
- Majumdar, D., Dutta, C., Mukherjee, A., Sen, S., 2008. Source apportionment of VOCs at the petrol pumps in Kolkata, India; exposure of workers and assessment of associated health risk. *Transp. Res. D Transp. Environ.* 13 (8), 524–530.
- Marchand, A., Aranda-Rodriguez, R., Tardif, R., Nong, A., Haddad, S., 2015. Human inhalation exposures to toluene, ethylbenzene, and m-xylene and physiologically based pharmacokinetic modeling of exposure biomarkers in exhaled air, blood, and urine. *Toxicol. Sci.* 144 (2), 414–424 Apr.
- Masih, A., Lall, A.S., Taneja, A., Singhvi, R., 2018. Exposure levels and health risk assessment of ambient BTX at urban and rural environments of a terai region of northern India. *Environ. Pollut.* 242 (Pt B), 1678–1683. <https://doi.org/10.1016/j.envpol.2018.07.107>. Nov.
- Pellizzari, E., Wallace, L.A., Gordon, S., 1992. Elimination kinetics of volatile organics in humans using breath measurements. *J. Expo. Anal. Environ. Epidemiol.* 2 (3), 341–356.
- Ras, M.R., Borrull, F., Marcé, R.M., 2009. Sampling and preconcentration techniques for determination of volatile organic compounds in air samples. *Trac. Trends Anal. Chem.* 28 (3), 347–361.
- Raysoni, A.U., Stock, T.H., Sarnat, J.A., Chavez, M.C., Sarnat, S.E., Montoya, T., Holguin, F., Li, W.W., 2017. Evaluation of VOC concentrations in indoor and outdoor micro-environments at near-road schools. *Environ. Pollut.* 231 (Pt 1), 681–693. <https://doi.org/10.1016/j.envpol.2017.08.065>. Dec.
- Rosén, G., Andersson, I.M., Walsh, P.T., Clark, R.D., Säämänen, A., Heinonen, K., Riipinen, H., Pääkkönen, 2005. A review of video exposure monitoring as an occupational hygiene tool. *Ann. Occup. Hyg.* 49 (3), 201–217.
- Salem, E., El-Garawani, I., Allam, H., El-Aal, B.A., Hegazy, M., 2018. Genotoxic effects of occupational exposure to benzene in gasoline station workers. *Ind. Health* 56 (2), 132–140 Apr 7.
- Santiago, F., Alves, G., Otero, U.B., Tabalipa, M.M., Scherrer, L.R., Kosyakova, N., Ornellas, M.H., Liehr, T., 2014. Monitoring of gas station attendants exposure to benzene, toluene, xylene (BTX) using three-color chromosome painting. *Mol. Cytogenet.* 7 (1), 15 Feb 27.
- Scheepers, P.T.J., Konings, J., Demirel, G., Gaga, E.O., Anzion, R., Peer, P.G.M., Dogeroglu, T., Ornekten, S., Van Doorn, W., 2010. Determination of exposure to benzene, toluene and xylenes in Turkish primary school children by analysis of breath and by environmental passive sampling. *Sci. Total Environ.* 408 (20), 4863–4870.
- Stojić, A., Maletić, D., Stanišić Stojić, S., Mijić, Z., Šoštaric, A., 2015 Jul 15. Forecasting of VOC emissions from traffic and industry using classification and regression multi-variate methods. *Sci. Total Environ.* 521–522, 19–26. <https://doi.org/10.1016/j.scitotenv.2015.03.098>. Epub 2015 Mar 28.
- Thomas, K.W., Pellizzari, C., Clayton, C.A., Peritt, R.L., Dietz, R.N., Goodrich, R.N., et al., 1993. Temporal variability of benzene exposures for residents in several New Jersey homes with attached garages or tobacco smoke. *J. Expo. Anal. Environ. Epidemiol.* 3, 49–73.
- Tunsaringkarn, T., Suwansakri, J., Soogarun, S., Siri Wong, W., Rungsiyothin, A., Zupuang, K., Robson, M., 2011. Genotoxic monitoring and benzene exposure assessment of gasoline station workers in metropolitan Bangkok: sister chromatid exchange (SCE) and urinary trans, trans-muconic acid (t,t-MA). *Asian Pac. J. Cancer Prev. APJCP* 12 (1), 223–227.
- Tunsaringkarn, T., Siri Wong, W., Rungsiyothin, A., Nopparatbundit, S., 2012. Occupational exposure of gasoline station workers to BTEX compounds in Bangkok, Thailand. *Int. J. Occup. Environ. Med.* 3 (3), 117–125 Jul.
- Weisel, C., Lawryk, N.J., Li, P.J., 1992. Exposure to emissions from gasoline within automobile cabins. *J. Expo. Anal. Environ. Epidemiol.* 2, 79–96.
- Weisel, C.P., 2010. Benzene exposure: an overview of monitoring methods and their findings. *Chem. Biol. Interact.* 184 (1–2), 58–66.
- Zoleikha, S., Mirzaei, R., Rokhsana, M., 2017. Exposure to chemical hazards in petrol pumps stations in Ahvaz City, Iran. *Arch. Environ. Occup. Health* 72 (1), 3–9.
- Ceypetco (2019) Ceylon Petroleum Corporation. Ceypetco product specifications. Accessed July 23th 2019 <http://ceypetco.gov.lk/ceypetco-products/>.
- Video Imaging and Data Interfacing and Analysis. <https://www.arbeidshygiene.nl/uploads/files/insite/sessie-l-pdf-paul-scheepers.pdf>, VIDITA v1.0, Accessed date: 24 August 2019.
- Tools for the practicing industrial hygienist. IHSTAT. <https://www.aiha.org/get-involved/VolunteerGroups/Pages/Exposure-Assessment-Strategies-Committee.aspx>, Accessed date: 9 March 2019.
- TestOrganizer Software, V20.6, Accessed date: 1 March 2019.