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Traffic-related air pollution. A pilot exposure assessment in Beirut, Lebanon

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HIGHLIGHTS

- *t,t*-MA levels could distinguish between office and traffic policemen.
- DHBMA is more suitable than MHBMA as biomarker of exposure to 1,3-butadiene.
- Beirut traffic policemen are potentially at a high risk for diseases development.

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ABSTRACT

Traffic-related volatile organic compounds (VOCs) pollution has frequently been demonstrated to be a serious problem in the developing countries. Benzene and 1,3-butadiene (BD) have been classified as a human carcinogen based on evidence for an increased genotoxic and epigenotoxic effects in both occupational exposure assessment and *in vivo*/*in vitro* studies. We have undertaken a biomonitoring of 25 traffic policemen and 23 office policemen in Beirut, through personal air monitoring, assessed by diffusive samplers, as well as through the use of biomarkers of exposure to benzene and BD. Personal benzene, toluene, ethylbenzene, and xylene (BTEX) exposure were quantified by GC–MS/MS, urinary trans, trans-muconic acid (*t,t*-MA) by HPLC/UV, S-phenyl mercapturic acid (S-PMA), monohydroxy-butenyl mercapturic acid (MHBMA) and dihydroxybutyl mercapturic acid (DHBMA) by ultra-performance liquid chromatography-electrospray tandem mass spectrometry (UPLC/ESI(-)-MS/MS) in MRM (Multiple Reaction Monitoring) mode. We found that individual exposure to benzene in the traffic policemen was higher than that measured in traffic policemen in Prague, in Bologna, in Ioannina and in Bangkok. *t,t*-MA levels could distinguish between office and traffic policemen. However, median MHBMA levels in traffic policemen were slightly elevated, though not significantly higher than in office policemen. Alternatively, DHBMA concentrations could significantly distinguish between office and traffic policemen and showed a better correlation with personal total BTEX exposure. DHMBA, measured in the post-shift urine samples, correlated with both pre-shift MHMBA and pre-shift DHMBA. Moreover, there was not a marked effect of smoking habits on DHBMA. Taken together, these findings suggested that DHBMA is more suitable than MHBMA as biomarker of exposure to BD in humans. Traffic policemen, who are exposed to benzene and BD at the roadside in central Beirut, are potentially at a higher risk for development of diseases such as cancer than office policemen.

1. Introduction

Traffic-related volatile organic compounds (VOCs) pollution has frequently been demonstrated to be a more serious problem in the developing countries than in the United States and Europe, as indicated by the VOC data obtained in Thailand, India, Pakistan and Egypt (Arayasiri et al., 2010; Rekhadevi et al., 2010; Kamal et al.,

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2012; Ibrahim et al., 2012). In Beirut, capital of Lebanon, air pollutant concentrations currently exceed air quality standards and guidelines (Waked and Afif, 2012). About 67% of non-methanic VOC emissions are calculated to originate from the on-road transport sector and the majority of vehicles operate on gasoline (Waked and Afif, 2012).

Since concentrations of VOCs are elevated, albeit to different extents, on and near roadways, the individuals whose job requires that they spend long periods of time near vehicles may incur substantial occupational exposures to traffic-related air pollution (Knibbs and Morawska, 2012). It is well known that exposure data from stationary monitoring sites cannot give the real exposure profile in urban areas, since the level of traffic VOCs decreases drastically as the distance from the main traffic roads increases (Han and Naeher, 2006). More and until now, no studies have been conducted to assess of the human health risks from urban air pollution exposure in Beirut. Taken together, we carried out a personal exposure measurement campaign among traffic policemen to benzene and 1,3-butadiene (BD), since both compounds are generated from the incomplete combustion of gasoline.

Benzene and BD have been classified as Group 1 carcinogens (IARC; 2008, 2009) based on evidence for an increased genotoxic and epigenotoxic effects in both occupational exposure assessment (Ruchirawat et al., 2010; Carugno et al., 2012; Peluso et al., 2012; Seow et al., 2012; Xiang et al., 2012) and in *in vivo* and *in vitro* studies (Dagher et al., 2006; Billet et al., 2010; Koturbash et al., 2011; Sangaraju et al., 2012; Tabish et al., 2012; Abbas et al., 2013).

Biomarkers of benzene, as urinary trans, trans-muconic acid (*t,t*-MA) and urinary S-phenylmercapturic acid (S-PMA), have been measured mostly in fuel-related exposure such as in station attendants, in public transportation or in traffic policemen (Fustinoni et al., 2005; Barbieri et al., 2008; Manini et al., 2010), while only a few studies of traffic-related exposures to BD have been performed (Sapkota et al., 2006; Arayasiri et al., 2010).

Although, BD is a known human carcinogen emitted from mobile sources, little is known about traffic-related human exposure to this toxicant. BD is metabolized *in vivo* to reactive epoxides which are supposedly responsible for the observed carcinogenic effects (category 1A; EU-RAR 2002). A main metabolic pathway for these epoxides is the reaction with glutathione, leading to a urinary excretion of 3,4-dihydroxybutyl mercapturic acid and 3-monohydroxybutenyl mercapturic acids (DHBMA and MHBMA). Up to now, DHBMA and MHBMA have already been used in population surveys as a biomarker of exposure to BD (Arayasiri et al., 2010; Ruchirawat et al., 2010; Cheng et al., 2012).

Hence, it will be of great interest to conduct a biomonitoring pilot study in order to assess traffic-related VOCs in central Beirut, and to evaluate the use of biomarkers of benzene and BD exposure of urban traffic policemen. This work was, therefore, undertaken to determine *t,t*-MA, SPMA, MHBMA and DHBMA in urine spot samples before and at the end of a working shift, and personal air monitoring to airborne benzene, toluene, ethylbenzene, and xylene (BTEX) during the work shift. The influence of personal exposure, job activity and personal characteristics on biomarkers excretion was evaluated.

2. Materials and methods

2.1. Measurements campaign design

The campaign took place during May-June 2011 and included measurements of BTEX personal exposure to 47 healthy volunteers. All participants were males. The volunteers group includes 24 traffic policemen and 23 office policemen which constitute the control group. The traffic policemen group consisted of officers whose activity consists exclusively of traffic regulation at intersections of central roads in the city. All participants were carrying passive samplers for BTEX during the working hours.

All participants kept a questionnaire requesting information about lifestyle and health status and a personal daily questionnaire, where they referred to the duration of the performed activities during sampling time.

2.2. Sample collection

The sampling was conducted on Monday, which is the first day of the work week after a two days holiday over the weekend to minimize residual exposure from the previous week. The work shift was 7 h d^{-1} and 5 h d^{-1} for traffic and office policemen, respectively. Individual air samples were attached to the clothing in the breathing zone of study subjects and throughout the entire work shift. After air sampling was completed, samples were capped, transported to the laboratory, and stored at 4 °C until analysis within 8 d by the end of the sampling campaign. Urine samples were collected at both pre-shift and post-shift and stored at −80 °C until analysis. All participants gave their informed consent and the study was approved by the Ethics Committee of the Lebanese University.

2.3. Analysis of BTEX

BTEX compounds were analyzed as described previously by Avogbe et al. (2011). Exposure to airborne BTEX was assessed by using GABIE (Gas Adsorbent Badge for Individual Exposure) diffusive samplers (ARELCO, ARC20001UP, France) containing activated charcoal cartridge. After sampling, the badges were sealed, preserved at −80 °C and sent for analysis to the "Centre Commun de Mesure", ULCO, Dunkerque (France). Briefly, BTEX were desorbed from the activated charcoal by using 2 mL of benzene-free carbon disulfide (Sigma, France) under agitation for 15 min. The mixture was filtered and 1 μL of the filtrate was analyzed on a Gas Chromatograph (GC) (CP-3800, Varian USA) coupled to a Mass Spectrometer (1200 TQ, Varian USA) using Factor four VF-5 ms column (0.25 mm internal diameter, 30 m, film thickness 0.25 μm). The carrier gas was helium, and the flow rate was set at 1 mL min^{-1}. The GC oven was held at 40 °C for 5 min and then increased to 310 °C at the rate of 5 °C min^{-1}. The recovery rate of extraction of benzene was 99%. Data were averaged over each sampling period.

2.4. Determination of urinary metabolites

2.4.1. Urinary t,t-muconic acid (t,t-MA)

Urine samples were thawed at room temperature for 15 min with frequent stirring, and then centrifuged at 3000*g* for 10 min. Aliquots of alkalinized urine were applied to a strong anion exchange (SAX 500 mg 3 cc) column (Varian) and subsequently washed with 3 mL 1% (v/v) acetic acid. The *t,t*-muconic acid was eluted with 3 mL 10% (v/v) aqueous acetic acid and then analyzed by HPLC equipped with a UV detector (Waters, Milford, USA). The concentration of *t,t*-MA was expressed as μg g^{-1} creatinine. The limit of detection (LOD) was 3 μg L^{-1}. The limit of quantification (LOQ) was 10 μg L^{-1}. The coefficient of variation of the method was within 12% for inter-day determination.

2.4.2. Urinary S-phenylmercapturic acid (S-PMA)

Four hundred microliters of urine containing 10 μL of deuterated internal standards at 10 μg mL^{-1} were added to 0.400 mL of sodium acetate buffer at 10 mM and 1 mL of distilled water. Sample mixture was homogenized for 0.5 min and centrifuged at 5000 rpm for 5 min. The supernatant was loaded onto Oasis®