Environmental Exposure to Volatile Organic Compounds among Workers in Mexico City as Assessed by Personal Monitors and Blood Concentrations

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Benzene, an important component in gasoline, is a widely distributed environmental contaminant that has been linked to known health effects in animals and humans, including leukemia. In Mexico City, environmental benzene levels, which may be elevated because of the heavy traffic and the poor emission control devices of older vehicles, may pose a health risk to the population. To assess the potential risk, portable passive monitors and blood concentrations were used to survey three different occupational groups in Mexico City. Passive monitors measured the personal exposure of 45 workers to benzene, ethylbenzene, toluene, o-xylene, and m/p-xylene during a work shift. Blood concentrations of the above volatile organic compounds (VOCs), methyl tert-butyl ether, and styrene were measured at the beginning and the end of a work shift. Passive monitors showed significantly higher (p < 0.0001) benzene exposure levels among service station attendants (median = 330 µg/m³; range 130–770) as compared to street vendors (median = 62 µg/m³; range 49–180) and office workers (median = 44 µg/m³, range 32–67). Baseline blood benzene levels (BBLs) for these groups were higher than those reported for similar populations from Western countries (median = 0.63 µg/L, n = 24 for service station attendants; median = 0.30 µg/L, n = 6 for street vendors; and median = 0.17 µg/L, n = 7 for office workers). Nonsmoking office workers who were nonoccupationally exposed to VOCs had BBLs that were more than five times higher than those observed in a nonsmoking U.S. population. BBLs of participants did not increase during the work shift, suggesting that the participants were chronically exposed to benzene, complex pharmacokinetic mechanisms were involved. Our results highlight the need for more complete studies to assess the potential benefits of setting environmental standards for benzene and other VOCs in Mexico. Key words: benzene, blood benzene levels, Mexico, personal exposure, volatile organic compounds, worker. Environ Health Perspect 107:511–515 (1999). [Online 12 May 1999] http://ehpnet1.niehs.nih.gov/docs/1999/107p511-515romieu/abstract.html

Benzene is a ubiquitous component in the environment that has been linked to adverse health effects, particularly leukemia and other cancers, even at low-dose exposures (1–4). Exposure assessment studies have indicated that important microenvironments for benzene exposure are those associated with smoking and gasoline use (e.g., driving, working at or visiting a service station, and having an attached garage) (5). One way to assess exposure is to use personal monitors that will integrate an individual’s benzene exposure over a specific period. However, for risk assessment purposes, it is important to measure biomarkers, such as blood benzene concentrations, that can provide information on the internal dose received by individuals. In turn, this dose can be related to health outcomes.

Mexico City is known for its air pollution problem, which is primarily related to vehicular traffic (6). In recent years, air monitoring in the downtown area has registered ambient benzene concentrations that represent a health concern [annual hourly mean of 45.4 µg/m³ (14.2 ppb) in 1995 and 46.4 µg/m³ (14.5 ppb) during the first 6 months of 1996]. Therefore, we conducted this study to evaluate individual exposures and blood concentrations of benzene and other volatile organic compounds (VOCs) in residents of Mexico City working in the downtown area.

Methods

Study population. The study population consisted of 45 volunteer men working in downtown Mexico City; 27 were service station attendants, 8 were street vendors who spend their entire workday outdoors, and 10 were office workers. The sample was selected to represent three exposure levels: high (service station attendants), medium (street vendors), and low (office workers).

Participants were not recruited randomly because the study was considered to be exploratory. Ideally, the sample should have included only nonsmokers; however, we were unable to recruit a sufficient number of volunteers. In our sample, half the participants reported being light smokers (n = 23). Fifty-two percent of service station attendants reported smoking (1–10 cigarettes/day); among these, 70% smoked ≤ 5 cigarettes/day. Among street workers, 50% reported smoking, but none reported smoking more than 2 cigarettes/day. Among office workers, 40% reported smoking, but none more than 3 cigarettes/day. Participants were asked to sign a consent form and to complete a questionnaire providing information on their sociodemographic characteristics and on their potential for exposure to VOCs.

Individual exposure during a work shift was measured with passive organic vapor badges (3M Company, Minneapolis, MN, and Pro-Tek, duPont, Newark, DE). Some workers started work early in the morning, making it difficult to attach the personal badges to all participants before the start of their work shift. However, all badges were attached within 2 hr after the participants began working. On average, each participant wore the badge for 6 hr. Badges were recovered within 1 hr after the end of the
work shift, sealed, and until analysis, kept at 4°C in a container with activated charcoal to avoid contamination with background levels. During the sampling time, participants were asked to avoid smoking and to minimize exposure from environmental tobacco smoke. Each participant provided one blood sample at the time the badge was attached and another at the time the badge was removed. The blood samples were obtained by venipuncture and collected into vacutainer tubes (Becton Dickinson, Rutherford, NJ) containing a mixture of potassium oxalate and sodium fluoride. These tubes had been previously treated to remove VOC contaminants and examined to verify that the contaminants had been adequately removed. Blood samples were kept at 4°C until shipment and analysis.

**Laboratory analyses.** The badges were analyzed for aromatic hydrocarbons using a method similar to the one employed by Fung and Wright (7). The charcoal strip was removed from the badge and placed in a 2-mL septum vial to which 1 mL of purified carbon disulfide was added. After ultrasonication for approximately 30 min, an aliquot of the extract was injected into the gas chromatograph (GC) for analysis. Recent improvements to the chromatographic method incorporate two-dimensional gas chromatography to allow large volumes (up to 10 µL) of sample extract to be injected, thus improving the sensitivity and selectivity of the method. The revised method has been fully described elsewhere (8).

Briefly, a 2 x 3 mm inner diameter (i.d.) packed coiled precolumn of 10% 1,2,3-tris(cyanoethoxy)propane (TCEP) on Chromosorb W (AnaLabs, Norwalk, CT) prepreared the solvent from the aromatic fraction of the injected aliquot. A 6-port valve switched the effluent from the precolumn to vent or to a cryogenic loop for trapping and focusing of the aromatic fraction. The loop was kept at -180°C with liquid N₂. Subsequently, the loop was electrically flash-heated to inject the compounds onto the analytical column for further separation and detection by a flame ionization detector. The analytical column was a 10 m x 0.25 mm i.d. 007-624 coiled capillary column (Quadrex Corp., New Haven, CT). Despite the large volume of sample injected, the calibration curve for benzene was linear (r² = 0.99994) in the range tested, 0.2–16 µg/mL. The benzene concentrations observed for the badge extracts were well within this range. The results for other aromatic compounds were similar. The revised method has high sensitivity and analytical precision, as demonstrated by the results from the 1992 California Residential Indoor Air Quality Study (8). Passive badge samples were analyzed by the laboratory on a blind basis. The benzene results on 10 pairs of duplicate (collocated) samples showed a regression slope of 1.03, with 0.00 intercept and a correlation coefficient, r² = 0.99 (9). Gravimetrically prepared standard solutions were injected before and after each set of samples analyzed. Ten percent of the sample extracts were also reanalyzed to establish analytical precision. Approximately 10% collocated samples and blanks were collected throughout the study. The standard deviations (SD), based on duplicate measurements of benzene in samples and blanks, were 0.051 µg and 0.097 µg, respectively. These results correspond to a lower quantifiable limit of 0.9 parts per billion volume (ppbv) benzene (at three times the standard deviation of the blank, accounting for the variability of the sample mass and volume) (10).

**Blood analysis.** Blood samples were stored and shipped refrigerated to a laboratory at the Centers for Disease Control and Prevention (CDC) for analysis. Samples were analyzed by purge-and-trap gas chromatography using isotope dilution mass spectrometry as described by Ashley et al. (11). Each sample was spiked with stable isotopes for each of the analytes examined. Samples were heated to 30°C, helium purged for 15 min, and then trapped on Tenax (Tekmar-Dohrmann, Cincinnati, OH). Absorbed water was removed from the Tenax trap by dry purging with helium for 6 min. The trap was then thermally desorbed at 180°C for 4 min and the VOCs were cryogenically trapped at the GC injection port. The analytes were injected onto the GC column by heating the cryogenic trap. Separation on a DB-624 capillary column (J & W Scientific, Folsom, CA) was followed by high-resolution mass spectrometric detection (full scan, 40–200 atomic mass unit, 1 scan/sec). Quantitation was accomplished by measuring specific ion responses from the unknown sample relative to those from the isotopically labeled analogs based on a six-point calibration curve. The limits of detection (LODs) for the different analytes were: 0.030 µg/L for benzene, 0.092 µg/L for toluene, 0.020 µg/L for ethylbenzene, 0.040 µg/L for o-xylene, 0.033 µg/L for m/p-xylene, 0.050 µg/L for methyl tert-butyl ether (MTBE), and 0.019 µg/L for styrene. Accuracy was assessed based on the analysis of spiked blood samples, and the estimated precision was ±20% relative standard deviation. Laboratory blanks were prepared from a water source shown to be VOC free, and vacutainers were specifically prepared to remove any contamination by VOCs (12). Storing samples for up to 7 weeks does not have a measurable effect on the analyses reported here (13). Ashley also analyzed the blood samples for most of the studies used for comparison. The other authors used a similar method based on headspace analysis rather than purge-and-trap. Compared to headspace analysis, the purge-and-trap method more completely removes volatile analytes from the sample, resulting in improved LODs. Ashley has participated in interlaboratory comparisons with other researchers to assure similar results from the two methods (14).

**Statistical analysis.** Data were analyzed using Stata software (15). Results are presented for participants who had two blood samples analyzed (beginning and after work shift) in addition to badge measurements. For badges, geometric mean and median concentrations of benzene, ethylbenzene, o-xylene, m/p-xylene, and toluene were determined in the total sample and stratified by working group. Similarly, for blood samples, geometric mean and median levels of the above compounds and of MTBE and styrene were determined and stratified by working group, and within group, by smoking status. Seven participants had missing values for VOC blood concentrations either because insufficient blood sample was collected (n = 4) or because participants provided only one blood sample (n = 3). The distribution of VOC blood concentrations was skewed to the right. After testing to determine the best transformation for normalizing the distribution (based on the Shapiro and Wilk test) (16), log transformation was used to normalize the blood data. The F-test was used to compare the mean VOC levels of the three groups and to compare beginning and postshift VOC blood concentrations. Spearman's rank correlation coefficients were calculated between the mean badge concentrations and the mean blood benzene levels (BBBs) among the different groups of workers (16).

**Results**

Badges were exposed for 6 hr on average (ranging from 4 to 8 hr). Personal badges measured exposure levels for benzene, ethylbenzene, o-xylene, m/p-xylene, and toluene, as presented in Table 1. The overall geometric mean (GM) for benzene exposure was 170 µg/m³. Benzene exposure levels among the service station attendants (GM = 310 µg/m³) were significantly higher (p < 0.0001) than those among the street vendors (GM = 77 µg/m³) or the office workers (GM = 44 µg/m³). A similar trend was observed for ethylbenzene, m/p-xylene, and o-xylene. However, toluene levels from personal badges were higher among office workers than among street vendors (p = 0.02).
A summary of the blood sample results is presented in Table 2. For the beginning shift, the overall median BBL was 0.54 µg/L. Again, the service station attendants had significantly higher BBLs (median = 0.63 µg/L, p < 0.001) compared to the two other groups. BBLs for the street vendors were significantly higher (median = 0.30 µg/L, p = 0.007) than BBLs for the office workers (median = 0.17 µg/L). Blood levels of ethylbenzene, o-xylene, m-/p-xylene, and MTBE were also highest among service station attendants, reflecting an increased exposure to gasoline. Toluene levels were similar for service station attendants and street vendors, but were significantly lower for office workers (p = 0.02). There was no significant difference in the blood levels of styrene among the three groups.

The overall median postshift BBL was 0.32 µg/L. Blood benzene concentrations were significantly higher among service station attendants (median = 0.42 µg/L, p < 0.001) compared to workers in the two other groups (medians for street vendors and office workers are 0.23 µg/L and 0.14 µg/L, respectively) (Table 2). Postshift concentrations of other VOCs, with the exception of styrene, were also highest among service station attendants. Styrene levels were similar for the three groups. Figure 1 presents a box plot of VOC levels measured in badges and in blood samples (at the beginning and end of the work shift) for each participating group.

Although our population included smokers, blood VOC levels were similar for smokers and nonsmokers, suggesting only light smoking among participants who did smoke. Stratifying the beginning shift data by smoking status resulted in comparable median BBLs among smoking (n = 12) and nonsmoking (n = 13) service station attendants (0.65 µg/L vs. 0.62 µg/L). Additionally, low levels of styrene and 2,5-dimethylfuruan in all of the subjects agree with the suggestion of minimal exposure from cigarette smoke. Cigarette smoke, in contrast to gasoline, is a significant source of exposure to styrene, and 2,5-dimethylfuruan has been used as a marker for smoking (17).

We calculated the correlation between benzene exposures measured by the personal samplers and postshift BBLs. For all three groups, the correlation was poor (r = 0.25 among service station attendants, r = 0.21 among street vendors, and r = 0.49 among office workers). However, these results must be interpreted with caution, given the small number of observations in the latter two groups.

Discussion
This study shows that in Mexico City, even residents who spend a large proportion of their time indoors and who are not occupationally exposed to benzene exhibit higher exposure levels than residents of countries studied by others. For nonoccupationally exposed office workers, personal exposure levels in ambient air during the work day ranged from 32 to 67 µg/m³ (GM = 44 µg/m³, SD = 13) for benzene. These levels are similar to the annual hourly mean reported in 1995 (6) for ambient air measurements in the downtown area of Mexico City, but are higher than those reported in other studies. The Total Exposure Assessment Methodology (TEAM) study, conducted by the U.S. Environmental Protection Agency in the United States, reported an overall mean personal exposure level for benzene of approximately 15 µg/m³ (4.7 ppb) in a sample of the general U.S. population. In contrast, the overall mean outdoor benzene concentration was only 6 µg/m³ (3). Other studies conducted in the United States have shown similar results, with daytime personal exposures ranging from 7.9 µg/m³ to 34.4 µg/m³ (5). In a study conducted in Germany among 113 subjects who wore personal samplers for 1 week, a mean exposure level of 10.5 µg/m³ with a maximum of 98 µg/m³ was observed (18).

Likewise, BBLs in all three working groups were higher than in nonoccupationally exposed U.S. populations. Specifically, office workers who were not occupationally exposed to VOCs had a beginning shift BBL (median = 0.17 µg/L) more than five times higher than a nonsmoking, nonoccupationally exposed population in the United States (19). Additionally, the toluene blood level (median = 0.71 µg/L) was more than three times higher; the median m-/p-xylene and ethylbenzene blood levels were more than two times higher; the median o-xylene blood level was approximately twice as high; and the styrene blood level was similar. Similar results were obtained when our data were compared.

Table 1. Personal badge concentrations (µg/m³) of benzene, ethylbenzene, o-xylene, m-/p-xylene, and toluene in workers from three occupational groups during their work shifts, Mexico City 1996.

| Pollutants         | Service station attendants (n = 24) | Street vendors (n = 6) | Office workers (n = 7) |
|--------------------|-------------------------------------|------------------------|------------------------|
|                    | GM    | Median | Range  | GM     | Median | Range  | GM     | Median | Range  |
| Benzene            | 0.31  | 0.30   | 0.23-0.70 | 0.08   | 0.08   | 0.06-0.25 | 0.10   | 0.10   | 0.08-0.21 |
| Ethylbenzene       | 0.47  | 0.47   | 0.45-0.54 | 0.37   | 0.37   | 0.34-0.40 | 0.46   | 0.46   | 0.43-0.50 |
| o-Xylene           | 0.42  | 0.42   | 0.40-0.45 | 0.39   | 0.39   | 0.37-0.42 | 0.41   | 0.41   | 0.39-0.45 |
| m-/p-Xylene        | 0.35  | 0.35   | 0.33-0.38 | 0.35   | 0.35   | 0.33-0.38 | 0.36   | 0.36   | 0.34-0.39 |
| Toluene            | 0.32  | 0.32   | 0.30-0.35 | 0.32   | 0.32   | 0.30-0.35 | 0.33   | 0.33   | 0.32-0.36 |
| MTBE               | 0.07  | 0.07   | 0.05-0.09 | 0.08   | 0.08   | 0.06-0.10 | 0.08   | 0.08   | 0.07-0.10 |
| Styrene            | 0.02  | 0.02   | 0.01-0.03 | 0.02   | 0.02   | 0.01-0.03 | 0.02   | 0.02   | 0.01-0.03 |

Table 2. Beginning and postshift blood concentrations (µg/L) of benzene, ethylbenzene, o-xylene, m-/p-xylene, toluene, and other volatile organic compounds (VOCs) among three groups of workers in Mexico City, 1996.

| Pollutants         | Beginning | Postshift |
|--------------------|-----------|-----------|
|                    | GM    | Median | Range | GM    | Median | Range |
| Benzene            | 0.33  | 0.30   | 0.26-0.68 | 0.37  | 0.37   | 0.26-0.70 |
| Ethylbenzene       | 0.33  | 0.33   | 0.29-0.63 | 0.38  | 0.38   | 0.28-0.70 |
| o-Xylene           | 0.30  | 0.30   | 0.27-0.60 | 0.36  | 0.36   | 0.28-0.70 |
| m-/p-Xylene        | 0.17  | 0.17   | 0.12-0.23 | 0.22  | 0.22   | 0.15-0.30 |
| Toluene            | 0.18  | 0.18   | 0.16-0.30 | 0.22  | 0.22   | 0.15-0.30 |
| MTBE               | 0.07  | 0.07   | 0.06-0.16 | 0.10  | 0.10   | 0.08-0.16 |
| Styrene            | 0.02  | 0.02   | 0.01-0.04 | 0.03  | 0.03   | 0.01-0.04 |

Abbreviations: GM, geometric mean; MTBE, methyl tert-butyl ether.

1. For service station attendants, n = 24 for benzene and ethylbenzene; n = 23 for o-xylene, MTBE, and styrene; and n = 25 for m-/p-xylene and toluene.
2. For street vendors, n = 5 for benzene, o-xylene, and m-/p-xylene and n = 6 for all other VOCs.
3. For office workers, n = 7 for benzene, n = 8 for toluene, and n = 10 for all other VOCs.

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to results from a nonsmoking subset of the National Health and Nutrition Examination Survey (NHANES) III population. In this NHANES subset, the median BBL was 0.047 μg/L and the median toluene BL was 0.21 μg/L (smoking was defined by serum cotinine levels > 10 ng/mL (14)). Brugnone et al. (20) reported a mean BBL of 0.17 μg/L among 243 normal subjects from the general Italian population; however, data were not provided on the smoking habits of these subjects. Although the current study included smokers, similar blood VOC levels among smokers and nonsmokers, coupled with low levels of styrene and 2,5-dimethylfuran, indicate little or no contribution to BBLs from smoking.

Blood benzene levels were significantly related to the working group. Service station attendants had BBLs twice as high as street vendors and more than three times higher than office workers. These findings are consistent with the results of previous studies. Moolenaar et al. (21) observed BBLs ranging from 0.45 to 3.23 μg/L among 13 automobile mechanics in Fairbanks, Alaska. In a study conducted among petroleum workers, Ong et al. (22) reported an arithmetic mean BBL ± SD of 6.04 ± 16.23 nmol/L (equivalent to 0.47 ± 1.27 μg/L). Brugnone et al. (20) reported a higher arithmetic mean BBL among 77 gasoline station attendants compared to a sample of 243 “normal” individuals (0.36 μg/L vs. 0.17 μg/L). In that study, BBLs in the morning preshift averaged 0.25 μg/L in winter and 0.43 μg/L in summer, both of which are slightly lower than that observed among service station attendants in this study (0.63 μg/L). Other VOCs, particularly MTBE, were also significantly higher in the blood samples of service station attendants than in the blood samples of the two other working groups (p < 0.001). Additionally, higher blood MTBE levels were found for service station attendants in this study compared to other studies (23,24).

In all three working groups, beginning shift BBLs were higher than postshift BBLs (Figure 1). However, none of the blood samples was actually taken before workers began the work shift. This fact is particularly important for service station attendants. Among this group, only one worker had a blood sample taken within 30 min of the start of the work shift. As expected, the beginning shift BBL in this case was lower (0.52 vs. 1.1 μg/L) than that at the end of the work shift. Additionally, the elapsed time between the end of the work shift and the collection of the blood samples impacted on BBLs. Postshift BBLs in blood samples drawn less than 10 min after the end of the shift were similar to samples drawn at the beginning of the work shift (n = 13; median = 0.60 vs. 0.57 μg/L). This result suggests that both beginning and postshift samples were drawn either at the peak of exposure or at similar points along the exposure curve. BBLs for postshift blood samples drawn more than 10 min after the end of the work shift (n = 11) were lower than beginning BBLs (median = 0.32 vs. 0.82 μg/L), suggesting that some of the benzene had already been metabolized or excreted. Investigation has shown that the VOC elimination phase is a multiphase process with a very short initial half-life of 1.6 min, an intermediate half-life of 10–60 min, and a longer half-life of 2–4 hr (25). Additionally, bioaccumulation in adipose tissues can occur as a result of repeated exposures of long duration. Such a complex pharmacokinetic mechanism for the elimination of benzene from tissues is likely to affect blood levels of VOCs at any particular time, making comparisons of acute versus chronic exposures difficult. This has been confirmed by Pekari et al. (26). In a study conducted among petrol station attendants, Brugnone et al. (20) reported BBLs that, during the winter, were 19% higher after the work shift as compared to the following morning and 34% higher during the summer. However, in a study conducted in Fairbanks, Alaska, Moolenaar et al. (23) observed that in three out of nine workers postshift BBLs were lower than beginning shift BBLs. For the two other groups of workers, postshift blood samples were collected less than 10 min after the end of the work shift so that postshift BBLs were only slightly lower than beginning shift BBLs.

The TEAM study (27) found that benzene levels in breath are about 0.17 times the exposure level in air (for nonsmokers). Blood/breath ratios were calculated based on this finding, which led to a blood/breath ratio of approximately 12 for the service station attendants and approximately 24 for the other two groups. These ratios are similar to those observed in comparable populations (5). Travis and Bowers (28) suggested that blood may contain a saturable component (e.g., proteins) that binds a limited amount of benzene, thus making it unavailable for distribution throughout the body (5).

The present study had some limitations inherent in its design and sample size. The inability to control for VOC exposure prior to the collection of the beginning-shift blood sample may have altered the results of the baseline data. In addition, among the group of service station attendants, 13 postshift blood samples were drawn after the workers had completed their work shift. A rapid decrease in BBLs following the end of exposure may have contributed to lower postshift values for these workers. For the two other groups in the current study, one possible explanation for lower postshift VOC levels is that the subjects may have been exposed to VOCs in public transportation before the beginning shift blood sample was drawn. Unfortunately, we do not have detailed activities of participants before the beginning shift sample was taken. Additionally, the cross-sectional design did not allow for a study of within-person variability in exposure or in blood concentrations.

Nonetheless, it is important to emphasize that BBLs observed among all the

Figure 1. Box plots of benzene concentrations measured in (A) blood and (B) badges (air concentration). In (A), blood concentrations are shown for each working group at the beginning and the end of the work shift. Shown are the median (center line in box), the 25th and 75th percentiles (i.e., the interquartile range: borders of the box), the range of values (vertical lines), and the outliers (circles).
workers studied were high, given that all the participants were either nonsmokers or light smokers. For nonoccupationally exposed office workers, personal exposure to benzene in ambient air during the workday ranged from 32 to 67 μg/m³ (mean a SD of 45 ± 13 μg/m³). Beginning shift BBLs of office workers ranged from 0.12 to 0.23 μg/L, with a median of 0.17 μg/L. These levels are higher than those reported in other studies. Based on data from Ashley et al. (19), the beginning shift BBLs observed for service station attendants, street vendors, and office workers correspond to smoking more than 30 cigarettes/day, 21–30 cigarettes/day, and almost 10 cigarettes/day, respectively.

The benzene content in Mexican fuel is only 1.5–2% (29), lower than that in Europe (2–6%) (4). MTBE content in Mexican fuel is 5% (29), lower than that in Alaska (15%) (21). Nevertheless, the personal exposures of the workers in this study were higher than those reported in other populations, most likely because of hydrocarbon emissions from heavy traffic density and the poor emission control of older vehicles. Indoor air, by virtue of air exchange, is also likely to be affected by motor vehicle exhaust and evaporative emissions. This study emphasizes the need for better control of hydrocarbon emissions as well as regulatory initiatives to reduce the exposure of workers and residents of Mexico City and other Mexican cities with heavy vehicular traffic.

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