

Atmospheric benzene and determination of trans, trans-muconic acid of workers at oil sites in Pointe-Noire.

ABSTRACT

Trans, trans-muconic acid is generally considered a useful biomarker of exposure to benzene that occurs naturally in crude oil. **Objective:** To estimate exposure of benzene to workers in an oil and gas production company. **Materials and methods:** Firstly, it was a descriptive, cross-sectional study which consisted to benzene atmospheric quantification in a sample individual measurements of homogeneous exposure group of workers. Secondly, urinary assays of trans, trans-muconic acid have been performed at the end of the shift in the selected workers. **Results:** A total of 79 (47.88%) workers agreed to participate in the study. Seventeen atmospheric samples were usable and 79 urinary assays at the end of the shift were carried out. The average benzene concentration for all sites was 10 times lower than the regulatory average exposure value (1 ppm=3.25 mg/m³): average: 0.122pp, median: 0.053ppm and range: 0.019-1.448 ppm. All 79 urinary assays of trans, trans-muconic acid were below the biological exposure index (<500 µg/g creatinine) with an average of 37.34 µg/g creatinine, a median of 30 µg/g creatinine, and an extent from 10 to 150 µg/g creatinine. **Conclusion:** Airborne benzene concentrations were below company limits. The same was true for the urinary assays of trans, trans-muconic acid. Overall, therefore, exposure to benzene is low in this company. However, there is a need to maintain regular medical surveillance as the risk of exposure is ongoing.

Keywords: benzene, metrology, trans, trans-muconic acid, oil site workers.

INTRODUCTION

The hematological toxicity of benzene is well known and established. Its toxic action on blood lines was suspected as early as 1897 by Lenoir and Claude, and its flattening effect was admitted as a compensable occupational disease in France from January 4, 1931. On the other hand, its proven leukemia effect led to its classification in the group of carcinogens (class 1 carcinogen) for humans by the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) in 1982 [1].

Occupational exposure to benzene occurs primarily in petrochemical industries (upstream and downstream), coke and steel plants, chemical and associated industries, and in research or analytical laboratories. Its main use is as an intermediate in the production of other chemicals, mainly ethylbenzene, cumene and cyclohexane. Benzene is also an important raw material for the manufacture of synthetic rubbers, gums, lubricants, dyes, pharmaceuticals and agricultural chemicals.

In industrial toxicology, urinary excretion of trans, trans-muconic acid (TTMA) is well correlated with external exposure to benzene in several studies in occupational subjects and as such, it is one of the metabolite currently considered to be biomarkers of workplace exposure to benzene [2].

In Congo, oil exploration and production began from 1960, but the literature review found no studies conducted among service stations, refineries staff, the oil terminal and workers in the onshore or offshore sites of different oil operators, notwithstanding that exposure of benzene and its analogues is a permanent risk at all petroleum sites in the country because benzene is a natural constituent of crude oil (0.4%) [3].

In addition, Congolese regulations also recognizes related disease to chronic exposure of benzene and its derivatives as occupational [4].

Therefore, in view of the findings described before, it appeared necessary to do in an oil exploration and production company which objective was to estimate exposure of benzene in workers directly exposed.

MATERIALS AND METHODS OF SURVEY

Setting, type and population of survey

The study was led by the Department of Occupational Medicine and all onshore and offshore sites of Total Exploration and Production Congo (TEPC), the leading oil company in Congo. This was an observational, descriptive cross-sectional study that took place from 1 October 2017 to 31 December 2017 either a period of 3 months.

The study population constituted of workers of the present the company, who were over 18 years of age and who had freely agreed to participate in the study, working in the external installations of oil sites with a risk of benzene exposure. The sampling technique was systematic and non-probabilistic. It means that the rules of selection have allowed to include in the consecutive ways a sample of operators and technicians working in all TEPC's onshore and offshore operational sites.

Study method:

The study was conducted in two (2) period:

First period: evaluation of atmospheric benzene using GABIE badges

The G.A.B.I.E (Gas Adsorbant Badge for Individual Exposure) is a passive sampler designed by the *Institut National de Recherche en Sécurité* (INRS) of France. It allows for:

- Passive sampling of gas such as BTX (Benzene, Toluene, Xylene),
- Air sampling in the respiratory area of personnel,
- Determination of the average concentration of these gas over a day working,
- The sample considers the professional gesture and the movements in the work area.

Organic compounds in the atmosphere are captured by diffusion. They are then trapped on an adsorbent material (active charcoal) at the bottom of the badge [5].

The badges were given to operators at the beginning of the shift and returned at the end of the shift after a period of 8 hours to 12 hours.

Wearing the badge does not influence the work by employees neither the preventive or protective measures setting up in the workplace (Figure n° 1, Ebatetou photo).

At the end of sampling, the badge is closed and stored at room temperature. Then, they were shipped as quickly as possible to an accredited laboratory in France, by plane and analyzing.

Benzene dosage was made by gas chromatography, which is a technical of molecules separation that make up a gas mixture.

The result is a concentration of vapors collected in ppm (or mg/m^3) reported over eight hours. These results show a good average representativity of the daily exposure and are valid for a group of persons belong to the same homogeneous exposure group (HEG). The 8-hour average exposure value (TWA) of benzene, in this oil company is 1 ppm (or $3.25 \text{ mg}/\text{m}^3$).

Second period: Urinary determination of trans, trans-muconic acid (TTMA)

Urine was collected from onshore and offshore sites at the end of shift and at the end of rotation.

2x5 ml of urine was collected from the workers concerned, from 2 specific tubes supplied by the testing laboratory.

After collection, the samples were stored in the freezer (-20°C) before being transported to France in a carboglace, in the hold, by plane.

The analysis was carried out in the same laboratory as the analysis of GABIE badges.

The biological analyses concerned liquid chromatography of trans, trans-muconic acid.

The determination of creatinuria was made by the Jaffe method. Results are rendered by $\mu\text{g}/\text{g}$ creatinine to account for diuresis. The reference value for the professionally exposed population (BEI) is $500 \mu\text{g}/\text{g}$ creatinine.

Study variables:

The various variables of the study were: socio-professional variables (sex, age, job held, place of work, work rhythm, seniority, concept of smoking), atmospheric concentration of benzene and urinary TTMA.

Operational definitions:

Operator or Technician

He is an oil worker working on an oil rig based at sea or on land. It carries out its activity in production or maintenance, contributing to the production of oil. The operator conducts his operations exclusively

in the external installations of the oil sites while the technician performs both in the external installations and in the control room which is in the neighborhood.

Homogeneous Exposure Group (HEG)

A HEG is a set of persons, positions or work functions for which exposure is of the same nature and intensity.

Onshore site

Onshore means exploration, research, drilling, onshore production, or onshore oil.

Offshore site

The offshore site refers to offshore oil platforms.

Statistical Analysis:

The data were entered and processed using Epi-info software version 7.2.2. The various tables and graphs were generated using Microsoft Office Excel 2016. For the quantitative variables, averages, medians and standard deviations were calculated. The χ^2 and Spearman correlation tests, were used to evidently put association links or to compare the different study variables.

Interpretation of the correlation coefficient r

- $r = 0,90$ to $1,00$ ($-0,90$ to $-1,00$): Very strong positive (negative) correlation
- $r = 0,70$ to $0,90$ ($-0,70$ to $-0,90$): positive (negative) correlation high
- $r = 0,50$ to $0,70$ ($-0,50$ to $-0,70$): Moderate positive (negative) correlation
- $r = 0,30$ to $0,50$ ($-0,30$ to $-0,50$): Low positive (negative) correlation
- $r = 0,00$ to $0,30$ ($0,00$ to $-0,30$): Negligible correlation

Differences were considered significant when p was less than or equal to 0.05 (<5%); 95% confidence intervals (5% margin of error) were calculated.

RESULTS

Socio-professional characteristics of the population

During the study period, 165 producers were operating on all TEPC operational sites. From the selection criteria that were defined, 79 operators or 47.88% were selected to constitute the sample

of the study. These were mainly workers operating primarily in the external installations of oil sites.

The workers were selected from five (5) sites of the six (6) operational sites available to TEPC.

These are the following:

- One (1) onshore site on one (1) (100%): Djeno oil terminal
- Four (4) out of five (5) offshore sites (80%): Alima, Nkossa, Yanga and Sendji.

Table I shows the breakdown of all workers selected according to their place of work.

The average age of producers was 33.3 ± 8.5 years, the median being 30 years, which is a relatively young population. The extreme ages were 25 and 60 years. The 30-39 age group was the most represented with 45 workers. All the workers were men.

The shift workers were either 8x8 days for those working in the onshore site or 14x14 days for those working in the offshore sites. The daily duration of the shift was 12 hours.

Average seniority was 9.4 ± 7.9 years, median 7 years and extremes 4 years and 36 years.

All reported cases of smoking were active and the average consumption of the overall smoking population was 1 pack/year.

All socio-professional characteristics are shown in Table II.

Benzene atmospheric metrology by GABIE badge

Of the 24 GABIE badges sent to the laboratory, 17 were usable and 7 had results below detection limits.

The different concentrations of benzene found at the study sites using the GABIE badges are shown in Table III.

A badge worn on the 17 usable had found a concentration of 1.448 ppm, higher than the average exposure value authorized on the company's sites (TWA= 1 ppm).

The average concentration of benzene at all sites was 0.12 ppm, the median 0.053 ppm, and the range 0.019-1.448 ppm.

Determination of trans, trans-muconic acid

Urine samples from the 79 workers of the study were all usable. The average level of TTMA in this study population was 37.34 µg/g creatinine. The median was 30µg/g creatinine with a range of 10-150 µg/g creatinine.

The Spearman correlation coefficient between worker ages and TTMA assays was -0.07 with a $p=0.52$ and a confidence interval of -0.29 to 0.16. On the other hand, that between their seniority and TTMA assays was -0.10 with a $p=0.36$ and a confidence interval of -0.321 to 0.13.

No link was found between smoking and TTMA levels in workers ($p=0.2726$). In addition, a statistically significant difference was observed in the relationship between the TTMA assay and the position of the worker because 38,5% of operators operating exclusively in the outdoor facilities of the sites had TTMA levels above 50µg/g creatinine compared to 17.5% of technicians operating both in the control room and outdoors ($p=0.0377$).

Atmospheric Benzene Correlation and T-Acid, T-MA

The Spearman r correlation coefficient between atmospheric benzene concentrations and TTMA assays in workers was 0.16 with a $p=0.149$ and a confidence interval of -0.066 to 0.377.

DISCUSSION

The population of this study was relatively young, with an average age of 33.27 ± 8.5 years and extremes of 25 and 60 years. Technicians and operators represent the lowest level of change in the category of workers at operational sites. These positions are usually filled by those who have recently been hired after a 2-year post-baccalaureate training. This finding is also observed by other authors who find middle ages below 40 years in oil workers: 30.8 years by Hofp et al in Norwegian offshore [6] and less than 40 years by Gardner in offshore installations of oil industries in Britain [7]. On the other hand, Bratveit et al, in Norway, in a study on benzene biometry among operators of an oil industry, had recovered an average age of 42.3 years [8].

This youth of the population is perfectly correlated with seniority at the post. In this work, 72.15% of workers had a seniority at the post of less than 10 years with an average of 9.4 years. However, in an American study of the risk of lymphohematopoietic cancers in 25,000 offshore workers exposed to benzene, the average seniority was less than 15 years [9].

The population included in this study was exclusively male. This could be explained, on the one hand, by the difficulty of being a technician or an operator, which requires considerable physical effort, and, on the other hand, by the isolation and exposure to chemicals which counter-indicate work in this environment to breastfeeding and pregnant women. In general, women are naturally excluded from these occupations as soon as they become pregnant for the first time. Hofp et al [6] and Kirkeleit et al [10] in Norway in their cohorts of workers at oil sites also had an exclusively male study population. On the other hand, in some studies, in offshore oil sectors, the authors found heterogeneous populations, although mostly male to more than 70% [8,11].

The oil sector is one of the sectors, such as the health sector, where activities must be maintained on an ongoing basis. Workers take turns at their shifts for 24 hours a day. In this work, 97% of the workers included had a shift work rhythm.

The notion of active smoking in this study was found in only 4% of workers. This concept is sought because tobacco smoke contains benzene [12]. In Hofp's work in Norway, 33.3% of workers were smokers [6] and 52% in a study on workers' exposure to benzene in Algeria [13]. The cultural characteristics of each population could be an explanation for the differences observed.

The exposure of workers to benzene at the various offshore and onshore sites of this company is a reality because benzene is a natural constituent of crude oil and therefore it is a permanent risk. To estimate the actual exposure to benzene in this working environment, reference is made to the measurements taken on working time (8 hours or 12 hours) and under normal conditions for the performance of the task. In this work, we used the passive GABIE badges of the INRS for the metrological study of benzene during working time. The GABIE badge is a passive badge that simplifies the measurement of exposures to gases and vapors in industrial atmospheres and allows the level of exposure to benzene and other volatile organic compounds to be defined over 8 working hours. It is therefore comparable to average exposure value [14,15].

Measurements of average air exposure levels at all sites (0.12 ppm) were below the average exposure value which is set at 1 ppm in this company. On the other hand, the analysis of a GABIE badge assigned to a producer working in an area of high concentration showed higher benzene concentrations equal to 1.448 ppm and therefore higher than the average exposure value. However, there is variability in exposure levels based on the sites, positions and tasks performed by workers.

The benzene vapor exposure data available in the literature relate to operations at offshore sites with values below the average exposure value and like those found in this study. During a regular activity in an offshore oil industry in Norway, the observed extent was 0.001-0.69 ppm [8]. In Bulgaria, Pesatori et al found an atmospheric benzene concentration in the range of 0.024 to 0.09 in a study of the early effects of low exposure to benzene among workers in an oil industry [11]. In Norway, Kirkeleit *et al*, in 2 different benzene exposure studies found average benzene levels of 0.02 ppm [16] and 0.23 ppm [10]; and Hopf *et al*, which evaluated exposure in offshore petroleum workers, found an average level of atmospheric benzene at 0.02 ppm [6].

S-phenylmercapturic acid is a biomarker of choice for benzene relative to its sensitivity for low ambient exposure to benzene [17-19]. All urinary assays of this biomarker performed at the end of the shift were lower than BEIs and can be considered as a reflection of very low producer exposure on the day of measurement. This finding, thanks to a biological marker, is consistent with the results of atmospheric sampling. The internal absorbed benzene dose appears to be low. These results are comparable to those described in the literature. These various studies carried out in the oil sector found in their study population very low and lower mercapturic acid concentrations than BEI [6, 10, 16, 17, 19,20].

In this work, no link was found between SPMA urinary assays on the one hand and on the other hand with the age of the producer, seniority at the post, the workplace, smoking, the concentration of benzene in the ambient air.

The very low level of exposure in the oil sites of this company, the limited sample of the study and the uniqueness of the measurements on a working day, could be an explanation for the lack of correlation between environmental measurements and biometry in this work. Moreover, the literature on work carried out at the crude oil production site [17,20] and at petrol stations [12, 21] finds a good correlation between S-acid levels on the one hand and SPMA and atmospheric benzene concentrations.

The lack of association between smoking and SPMA urinary assays in this work may be due to the very small number of smoking workers in our sample, comparisons under these conditions are not optimal. In contrast, urinary excretion of SPMA acid is known to increase with tobacco consumption [8]. In fact, Boogard et al, in a comparative study of benzene biometry in the Netherlands, found high levels of SPMA among smokers ($p < 0.001$) [17].

CONCLUSION

The estimate of benzene exposure for a subpopulation of workers at this oil company was made by this study. It appears that in normal operation, the exposure of technicians and operators to benzene is low because the data in atmospheric metrology and biometrology are well below occupational exposure limit values and biological indices all operational sites investigated notwithstanding variability by site and tasks performed.

Ultimately, this is an occupational group with low exposure to benzene. Furthermore, in view of the permanent presence of benzene at the various sites of this company, it is necessary to maintain the preventive measures already in place and to regularly monitor the health of potentially exposed workers.

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Table I: Distribution of workers by site

		Effective		Percentage
	Alima	11		
Off-shore	Nkossa	25		
	Sendji	5	53	67.09%
	Yanga	12		
On-shore	Djeno	26	26	32.91%
Total		79		

Table II: Distribution of workers by socio-professional characteristics

Features	Effective	%
Age (years)		

Under 30 years	27	34.2
30-40	45	57
Over 40 years	7	8.9
Sex		
Female	0	0
Male	79	100
Work Rythm		
Daytime	2	2.5
Shift work	77	97.5
Seniority at the post		
Less than 10 years	57	72.1
10-20	15	19
More than 20 years	7	8.9
Smoking		
Yes	3	4
No	76	96
Position Type		
Operator	39	49.4
Technician	40	50.6
Total	79	100

Table III: Concentration of atmospheric benzene by site

GABIE badge Number	Benzene concentration(ppm)	Average
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	1	0.053	
	2	0.024	
Djeno	3	0.019	0.31
	4	0.02	
	5	1.448	
	6	0.019	
Alima	7	0.054	0.036
	8	0.021	
	9	0.02	
Nkossa	10	0.02	0.02
	11	0.019	
	12	0.055	
	13	0.056	
Nord	14	0.053	
(Yanga-Sendji)	15	0.071	0.061
	16	0.064	
	17	0.066	

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Figure n ° 1: Wearing GABIE badge (Ebatetou photo)