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# Human risk assessment of benzene after a gasoline station fuel leak

# Avaliação de risco humano a benzeno após vazamento de combustível em posto de gasolina

#### **ABSTRACT**

**OBJECTIVE:** To assess the health risk of exposure to benzene for a community affected by a fuel leak.

**METHODS:** Data regarding the fuel leak accident with, which occurred in the Brasilia, Federal District, were obtained from the Fuel Distributor reports provided to the environmental authority. Information about the affected population (22 individuals) was obtained from focal groups of eight individuals. Length of exposure and water benzene concentration were estimated through a groundwater flow model associated with a benzene propagation model. The risk assessment was conducted according to the Agency for Toxic Substances and Disease Registry methodology.

**RESULTS:** A high risk perception related to the health consequences of the accident was evident in the affected community (22 individuals), probably due to the lack of assistance and a poor risk communication from government authorities and the polluting agent. The community had been exposed to unsafe levels of benzene (> 5  $\mu$ g/L) since December 2001, five months before they reported the leak. The mean benzene level in drinking water (72.2  $\mu$ g/L) was higher than that obtained by the Fuel Distributer using the Risk Based Corrective Action methodology (17.2  $\mu$ g/L). The estimated benzene intake from the consumption of water and food reached a maximum of 0.0091  $\mu$ g/kg bw/day (5 x 10<sup>-7</sup> cancer risk *per* 10<sup>6</sup> individuals). The level of benzene in water vapor while showering reached 7.5  $\mu$ g/m³ for children (1 *per* 10<sup>4</sup> cancer risk). Total cancer risk ranged from 110 to 200 *per* 10<sup>6</sup> individuals.

**CONCLUSIONS:** The population affected by the fuel leak was exposed to benzene levels that might have represented a health risk. Local government authorities need to develop better strategies to respond rapidly to these types of accidents to protect the health of the affected population and the environment.

DESCRIPTORS: Benzene, toxicity. Gasoline, adverse effects. Chemical Hazard Release. Chemical Accidents. Environmental Exposure. Water Pollution. Risk Assessment.

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# **RESUMO**

**OBJETIVO:** Avaliar os riscos à saúde da exposição ao benzeno de comunidade afetada por acidente de vazamento de combustível.

**MÉTODOS:** Dados de acidente de vazamento de combustível ocorrido em Brasília, DF, em 2002, foram obtidos dos relatórios produzidos pelo distribuidor de combustível e submetidos a autoridade ambiental. Informação sobre a população afetada foi obtida em grupos focais com oito participantes. Foram estimados o tempo de exposição e concentração de benzeno na água usando modelo de fluxo subterrâneo acoplado a outro de transporte. A avaliação de risco foi conduzida de acordo com a metodologia da Agência de Registro de Substâncias Tóxicas e Doenças (*Agency for Toxic Substances and Disease Registry*).

**RESULTADOS:** Alta percepção de risco à saúde relacionada ao acidente foi observada na população afetada (22 indivíduos), provavelmente devido à falta de assistência e à comunicação de risco deficiente do governo e agente poluidor. A comunidade esteve exposta a níveis inseguros de benzeno na água (> 5 μg/L) a partir de dezembro de 2001, cinco meses antes de ser reportado o vazamento. A concentração média de benzeno na água consumida (72,2 μg/L) foi maior que aquela estimada pelo distribuidor usando a metodologia Ação Corretiva Baseada em Risco (*Risk Based Corrective Action*) (17,2 μg/L). A ingestão estimada de benzeno pelo consumo de água e frutas alcançou 0,0091 μg/kg pc/dia (risco de 5 x 10<sup>-7</sup> câncer *per* 10<sup>6</sup> indivíduos). O nível de benzeno no vapor d'água durante o banho atingiu 7,5 μg/m³ para crianças (risco de câncer de até 1 *per* 10<sup>4</sup>). O risco carcinogênico total foi de 110 a 200 *per* 10<sup>6</sup> indivíduos.

**CONCLUSÕES:** A população afetada pelo vazamento de combustível esteve exposta a concentração de benzeno que pode ter representado risco à saúde. Autoridades governamentais necessitam desenvolver estratégias mais efetivas para rapidamente responder a esses acidentes e proteger a saúde da população afetada e do meio ambiente.

DESCRITORES: Benzeno, toxicidade. Gasolina, efeitos adversos. Vazamento de Resíduos Químicos. Acidentes Químicos. Exposição Ambiental. Poluição da Água. Medição de Risco.

# **INTRODUCTION**

The most significant sources of environmental contamination by hydrocarbons in urban areas are fuel leaks and/or spills at gasoline stations. <sup>4,13</sup> Fuel leaks occur mainly due to the lack of tightness in the fuel storage system, corrosion in the metal structures of the tanks and pipes, and inadequate operational procedures. <sup>9</sup> Hydrocarbons are the most frequently group of compounds found in contaminated areas, mainly benzene and toluene. <sup>17</sup> Benzene is a well known human carcinogen, with its action spreading throughout the entire hematologic system, causing depression of the bone marrow and pancitopenia, and has been frequently detected in occupationally exposed workers. <sup>a</sup>

The use of ethanol as a fuel or added to other fuels has proven to be a global trend. The addition of ethanol to gasoline has been subject to successive governmental regulation in Brazil, ranging from 18 to 25% (Law 12490/2011). In the event of a gasoline leak, the presence of ethanol increases the transfer of hydrocarbons to the liquid phase, increasing the concentration of contaminants in the groundwater. This process, known as cosolvency,<sup>6</sup> affects the transfer of the plume, reducing the natural biodegradation of the contaminants, and increasing their persistence in the groundwater. <sup>15,19</sup>

<sup>&</sup>lt;sup>a</sup> United States Department of Health and Human Services Public Health Service. Agency for Toxic Substances and Disease Registry. Toxicological profile for Benzene. Atlanta; 2007 [cited 2013 May 16]. Available from: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=40&tid=14

Methods of evaluating the risk of the presence of contaminants in the environment have been developed by the US Environmental Protection Agency,<sup>b</sup> by the Agency for Toxic Substances and Disease Registry (ATSDR)<sup>c</sup> and by the American Society for Testing and Materials that developed the Risk Based Corrective Action (RBCA) method.<sup>d</sup>

The RBCA method has been used in some Brazilian studies, e while the Ministry of Health, has recommended using the ATSDR methodology. The lack or absence of environmental and health data has hampered the assessment of human health risks in contaminated areas. Studies on environmental contamination and human exposure have been conducted for 2.7% of the Brazilian areas reported to have contaminated or potentially contaminated soil, mostly restricted to confirming the contamination of the groundwater, with no quantitative assessment of the exposure and risk.

This study aimed to assess the health risk to a community affected by a fuel leak reported in 2002 in the Federal District, Brazil

#### **METHODS**

Environmental data used to characterize the residential area affected by the fuel leak in the Brasilia, DF, 2002, and data on benzene levels in soil, groundwater and food grown in the area were obtained from nine reports produced by the Fuel Distributor (June 2002 to January 2003; not published) submitted to the Federal District's environmental agency, and from the gasoline station's licensing documentation. Soil samples were collected at 1-2 m deep and are not relevant to this study. Groundwater samples were collected between July and October 2002 from shallow well 1 (five samples), shallow well 2 (five samples) and shallow well 3 (four samples) (Figure 1), and analyzed according to the U.S.EPA Method 8260, using gas chromatography coupled to a mass spectrometer (GC/MS), with a limit of detection (LOD) of 1 µg/L. Benzene was analyzed in green mango and pitanga samples, collected in the residential area in November 2002, by GC/MS (U.S.EPA Method 5021; LOD of 1.0 µg/kg). Results of routine blood biochemical exams performed on several occasions between May 2002 and September 2004 were obtained from the affected community. A suspicion protocol considered individuals in a critical situation when biochemical alterations were observed in at least two consecutive exams over a period of 60 days.<sup>f</sup>

Two focal group sessions, with four individuals each, were conducted in 2007 to assess the concerns of the population of the affected community about the fuel leak. The individuals responded to a 20-item questionnaire, with questions on social and economic issues. The sessions were guided by the questions: How did you find out about the fuel leak?; What were the concerns and doubts you had during the leakage event?; How were these concerns and doubts addressed by the government and by the polluter?; What health problems did you associate with exposure?; What type of health care was provided?; What are your current doubts and concerns? The statements were recorded, transcribed without editing and grouped by specific theme according to the criteria of Rabiee. 16

This part of the study was approved by the Ethics Committee of the "Faculdade de Ciências da Saúde da Universidade de Brasilia" (Process nº 037/2007).

The collection of water samples from the shallow wells for analysis began in July 2002, two months after the accident was reported. The period of exposure and the benzene concentration in water were estimated using a time-space evolution of the contaminant plume by a tridimensional groundwater flow model coupled to a contaminant transport model. The modeling process used the Visual Modflow v 4.3.h The hydraulic parameters of the aquifer (hydraulic conductivity, specific storage and recharge) used for the flow model were obtained from the Fuel Distributor reports. An automatic calibration of the hydraulic parameters was performed for the best fitting of a time series of piezometric head values observed at the 29 installed monitoring wells (some shown in Figure 1). Calibration of the model was confirmed by comparing the response of the calibrated model with values observed at the 16 wells not used in the stage prior to calibration. The gradient that allowed

b United Sates Environmental Protection Agency. Exposure Factors Handbook: 2011 edition. Washington (DC); 2011 [cited 2013 May 16]. Available from: http://www.epa.gov/ncea/efh/pdfs/efh-complete.pdf

<sup>&</sup>lt;sup>c</sup> United States Department of Health and Human Services Public Health Service. Agency for Toxic Substances and Disease Registry. Public health assessment guidance manual (2005 Update). Atlanta; 2005 [cited 2013 May 16]. Available from: http://www.atsdr.cdc.gov/hac/phamanualindex.html

d American Society for Testing and Materials. Standard guide for risk-based corrective action applied at petroleum release sites. ASTM E-1739-95. Philadelphia; 2010. Available from http://enterprise.astm.org/filtrexx40.cgi?+REDLINE\_PAGES/E1739.htm

<sup>&</sup>lt;sup>e</sup> Michels C, Schneider MR, Coelho JIE, Corseuil HX. Avaliação de risco à saúde humana em terminais de armazenamento de petróleo e derivados: estudos de casos. In: Anais do XIII Congresso Brasileiro de Águas Subterrâneas, Cuiabá, BR. Cuiabá: Associação Brasileira de Águas Subterrâneas; 2004. v.1, p.1-12.

<sup>&</sup>lt;sup>f</sup> Ministério da Saúde. Diretrizes para Elaboração de Estudo de Avaliação de Risco à Saúde Humana por Exposição a Contaminantes Químicos. Brasília (DF); 2006. Available from http://portal.saude.gov.br/portal/arquivos/pdf/diretrizes\_avalicao\_risco.pdf

<sup>&</sup>lt;sup>8</sup> Bueno PC. Sistema de Informação de Vigilância em Saúde de Populações Expostas a Solo Contaminado (SISSOLO): análise dos dados de 2004 a 2008. Brasília (DF): Universidade de Brasília; 2008.

 $<sup>^{\</sup>rm h}$  Waterloo Hydrogeologic software package. Available from: http://www.software.com.br/visual-modflow.html?gclid=CIWRo7fQ3LcCFeNj7A odeGAAcQ

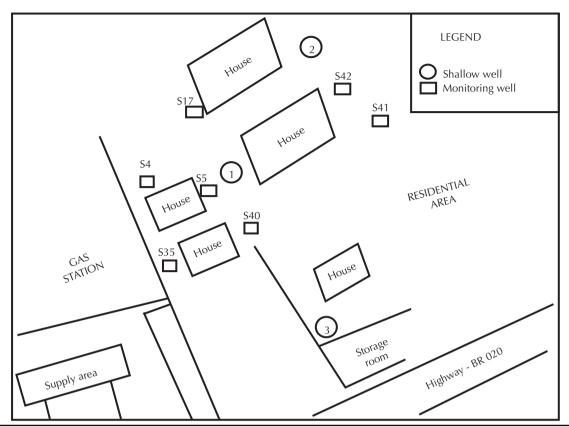


Figure 1. Water sampling points in the residential area affected by the fuel leak. Federal District, Brazil, 2002.

the migration of the light non-aqueous phase liquid (LNAPL) was determined month to month. LNAPL, such as gasoline and fuel oil, do not mix well with water and are less dense than water. 14 The geometry of the plume extracted from the Fuel Distributor reports was used to determine the mathematical contour conditions. The initial time for the transport model was determined through the inverse calculation based on the plume shapes for June 2002. The development of the benzene dissolved phase plume was simulated using the MT3DMS transport model present in the Visual Modflow interface. The shape of the LNAPL was used as mathematical boundary condition for the transport model. The contaminant transport model was calibrated in the inverse modeling using the benzene concentration found in shallow well 1 water samples collected at five sampling times in 2002 (July: 220 μg/L; August 09: 510 μg/L; September 24: 860 µg/L; October 30: 880 µg/L and November 05:1100 μg/L). The equilibrium concentration at the interface between the LNAPL and the dissolved phase was determined according to Corseuil and Fernandes.5

Five components of a complete exposure pathway need to be identified, according to the ASTDR methodology:

a source of contamination, a release mechanism, an exposure route (oral, dermal or inhalation), an exposure point, and a potentially exposed population.<sup>c</sup> The data available allowed the identification of four complete exposure pathways: water dermal contact, water consumption, fruit consumption and inhalation of water vapor during shower. In all cases, the source of contamination was the fuel station, the exposure point was the affected residential area and the potentially exposed population the residents of the affected area. The release mechanism to water and food was the fate and transport of environmental contamination.

The daily benzene exposure doses from the consumption of water and food and from dermal absorption by contact with the water were estimated using the standard equations in the ATSDR method.<sup>f</sup> To estimate the intake from consumption of water and food, a frequency of seven days/week and a time of exposure estimated by the model (water) wwere considered and during October 2002 for the fruits (beginning of the harvest period), for a exposure over an entire lifetime (70 years). Consumption data for mangoes were obtained from the Brazilian Personal Food Consumption data (consumers-only)<sup>i</sup> and one

<sup>&</sup>lt;sup>1</sup> Instituto Brasileiro de Geografia e Estatística. Pesquisa de Orçamento Familiar 2008/2009. Brasília (DF); 2011. Available from: http://www.ibge.gov.br/home/estatistica/populacao/condicaodevida/pof/2008\_2009/POFpublicacao.pdf

Table 1. Body weight, mean	consumption of fruit and water	: and body surface are	ea for estimating exposure	Federal District, Brazil

Age (years) Bo	Dadwariaht (lan)	Fruit (g/day)		Matau (L/day)b	Doducento co cuco (cuco)b	
	Body weight (kg) <sup>a</sup> —	Mango <sup>a</sup>	Pitanga	— Water (L/day) <sup>b</sup>	Body surface area (cm) <sup>b</sup>	
Up to 1	10	0	0	0	2,900	
1-11	25	168	100	0.5	8,000	
12-17	53	177ª	100	1	15,900	
≥ 18 (men)	73	131ª	100	1.5	20,375	
≥ 18 (women)	63	$140^{a}$	100	1.5	18,262/2,075°	

<sup>&</sup>lt;sup>a</sup> Instituto Brasileiro de Geografia e Estatística. Pesquisa de Orçamento Familiar 2008/2009. Brasília (DF); 2011. Available from: http://www.ibge.gov.br/home/estatistica/populacao/condicaodevida/pof/2008\_2009/POFpublicacao.pdf

daily serving of 100 g of *pitanga* was assumed for all individuals  $\geq 1$  year (Table 1). The water and food consumption by children < 1 year was considered to be zero, as nutrition needs relied only on breastfeeding. In the estimation of the exposure to benzene through water dermal contact, a 12-minute-exposure when bathing was considered, twice a day for children < 12 years, and once a day for adolescents and adults. An additional daily water exposure of two hours was considered for adult women for the contact of the hands and forearms during domestic work and handling of livestock and pets. Water permeability constant (25°C) was 0.18 cm/hour. Body weight, water consumption and surface data used in the estimates are also shown in Table 1.

The average concentration of benzene in the air while showering was estimated according to López et al<sup>13</sup> considering a 12-minute-shower, shower cubicle volume of 2,000 L, water temperature of 35°C, shower flow rate of 2.8 L/min, ventilation rate of 167 L/min and benzene Henry constant of 0.191. The mean concentration of benzene in the water was estimated by the inverse model.

This study was approved by the Ethics Committee of the "Faculdade de Ciências da Saúde da Universidade de Brasilia" (Process 037/2007).

#### **RESULTS AND DISCUSSION**

Residents of an area in the vicinity of a gasoline station about 30 km from Brasilia, DF, reported the existence of a strong odor in the water collected in shallow well 1, located approximately 73 meters from the gasoline station supply area (Figure 1) to the local environmental agency and media in May 2002. The Fuel Distributor (polluter) identified a leak in one of the diesel pipes of the underground fuel storage system. Volatile organic compounds, including BTEX (benzene, toluene, ethylbenzene and xylenes), were detected in the soil of the diesel discharge area (14,000 mg/kg), next to the gasoline pump (6,720 mg/kg) and in the area behind the gasoline

station that received untreated effluents (300 mg/kg). Benzene and other contaminants were detected in shallow well 1 and in the monitoring wells S4, S5 and S35 (Figure 1). Remediation actions were taken at the gasoline station to restrain the LNAPL in June 2002, and the community stopped drinking water from the shallow wells. Another spill occurred in September 2002 and the population was removed from the area in October 2002. when the remediation actions taken at the residential area were terminated, with the removal of 1.361 liters of gasoline and 50 liters of diesel. Remediation actions of the LNAPL at the gasoline station were finalized in December of the same year, with the removal of 1,575 liters of gasoline and 68 liters of diesel. The remediation of the dissolved phase in the groundwater was concluded in the residential area in January 2007, and has remained active at the gasoline station area up until the conclusion of this study.

The affected residential area covered nearly 2 ha and, at the time of the leak, 25 there were four brick houses, fruit trees, vegetable gardens, and chickens for local consumption. The water used for various purposes came from three shallow wells (Figure 1). Sewage was collected through a septic tank system, and solid waste was collected by the urban collection service. It was reported during the focal groups that the community in the residential area comprised 22 non-smoking individuals, 14 adults (≥ 18 years), five adolescents (12 to 17 years), two children (one to 11 years) and a male baby < 1 year. Half of the individuals were female and had college degrees, five held jobs and three were students. The predominant family income for this group was > 20 minimum monthly wage (MMW ~ US\$ 146.00) and one person had private health insurance.

The initial concerns regarding the leak presented by the participants of focal groups referred to losses related to life style in a rural setting:

"(...) our dream is over"; "(...) we built this house... we began to realize we were going to lose it... where would we go with a bunch of small children."

<sup>&</sup>lt;sup>b</sup> United States Environmental Protection Agency. Exposure Factors Handbook: 2011 Edition. Washington (DC); 2011 [cited 2013 May 16]. (EPA/600/R-090/052F). Available from: http://www.epa.gov/ncea/efh/pdfs/efh-complete.pdf

<sup>&</sup>lt;sup>c</sup> hands and forearms

An uneasiness that was later confirmed "(...) I had to leave my house."

Participants also manifested concerns associated with changes in health during the event:

"(...) itching... prostration... headaches... dizziness... nausea...wanting to vomit all the time... feeling bad... laziness (...) hypothyroidism... my period lasted almost 180 days... all the women gained weight (...) it was a total mental mess".

For one participant, exposure to benzene would cause "death or leukemia after 20 years of exposure".

The following statement reflects the sense of frustration of the group: "(...) I didn't ask for this, I don't want this. I didn't give anyone the right to do this to me." It became clear among the participants that there was "disregard" of the polluting agent and "lack of preparation" of the government authorities in addressing the problem, generating feelings of "indignation, helplessness, and abandonment".

The participants reported changes in health, both during the occurrence of the leak and afterwards, mainly headaches, nausea, weight gain, emotional changes, menstrual flow increase and prostration. It is possible that some of these symptoms were psychosomatic manifestations related to the emotional state and stress they were submitted to during the event. One mother stated that her baby, who was < 1 year at the time of the event, had lost weight and later had dental alterations.

Levels of benzene in five groundwater samples collected in shallow well 1 (Figure 1) ranged from 220 to 1,100  $\mu$ g/L, 44 to 220 times the Brazilian intervention and maximum levels of 5  $\mu$ g/L (CETESB, Regulation 518/2004, Ministry of Health). Shallow well 1 was the only water source used by the individuals from the residential area. Benzene was not detected in samples from shallow wells 2 and 3. The benzene concentration in groundwater found in this study were higher than those reported by Forte et al in a residential shallow well affected by a fuel tank leak in the Northern Brazil (34  $\mu$ g/L).

Benzene was detected in one sample of *pitanga* (254.4  $\mu$ g/kg)1and in one green mango sample (3.0  $\mu$ g/kg) collected in the residential area. The Fuel Distributor reports do not contain information on the total number of fruit samples analyzed. These levels are higher than those reported in fresh fruit from non-contaminated areas

(background level) ( $< 0.5 \mu g/kg$ ),<sup>20</sup> and are most likely due to soil contamination by the fuel tank leak.

The exposure to unsafe levels of benzene in the water (>  $5 \mu g/L$ ; Regulation 518/2004, Ministry of Health) estimated by the inverse model started on December 14 2001 (Figure 2). As the community stopped drinking the water in June 2002 and was removed from the area in October 2002, the community was exposed to benzene from water consumption for 195 days and from water dermal contact and water vapor inhalation for 315 days. The mean concentration of benzene in the water estimated by the model during the oral exposure period (range of 5.1 to 235.5  $\mu g/$ ) was 72.6  $\mu g/L$  (95%CI 40.9;104.2).

During the dermal and inhalation exposure period (ranging from 5.1 to 2,592 µg/L), the mean benzene concentration was 358.8 µg/L (95%CI 155.5;562.0). The 95th upper level confidence intervals (95th UCL) of the mean concentrations were used in the estimation of the exposure to contaminated water: 104.2 µg/L for consumption and 562 µg/L for dermal contact and inhalation. The mean benzene concentration in the air while showering, estimated according to López et al, 13 was 7.5 μg/m<sup>3</sup> for children (< 12 years) and 3.7 ug/m³ for adolescents and adults. Lindstrom et al12 found that benzene levels measured in the air from a gasoline-contaminated groundwater home containing 300 µg/L ranged from 758 to 1,670 µg/m<sup>3</sup> while showering, indicating that the López et al<sup>13</sup> equation may underestimate concentrations in air while showering.

Total oral exposure ( $TE_{oral}$ ) ranged from 0.0076 to 0.009 µg/kg bw/day, mostly due to water consumption (OE, ) (> 98% for all age groups), representing 0.19 to 0.23 % of the benzene chronic reference dose (RfD) of 4 μg/kg bw (non-cancer risk) (Table 2). The carcinogenic risks were estimated by multiplying the TE<sub>gral</sub> by the upper limit of the risk interval per 1 million people from the oral exposure to benzene (oral slope factor) of 5.5 x 10<sup>-5</sup>/µg/kg bw day.<sup>k</sup> Cancer risk ranged from  $4.2 \times 10^{-7}$  to  $5.0 \times 10^{-7}$  (Table 2). The specific cancer risk from the consumption of contaminated water was estimated by comparing the 95th UCL of the mean benzene concentration estimated by the inverse model during the oral exposure period (104.2 µg/L) with the specified risk levels established by the USEPA. The exposure represents the risk of 1 cancer per 104 inhabitants (within the range of 100 to 1000  $\mu$ g/L).<sup>k</sup>

Benzene doses from dermal exposure (DEw) ranged from 0.0056 to  $0.0130~\mu g/kg$  bw day (Table 2), higher for children and adult women due to the longer time

<sup>&</sup>lt;sup>1</sup> Companhia de Tecnologia de Saneamento Ambienta (BR). Decisão de Diretoria nº 195-2005- E, de 23 de novembro de 2005. Dispõe sobre a aprovação dos Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo – 2005, em substituição aos Valores Orientadores de 2001, e dá outras providências. *Diario Oficial Uniao*. 23 dez 2005 [cited 2013 May 16]. Available from: http://www.cetesb.sp.gov.br/Solo/relatorios/tabela\_valores\_2005.pdf

k United Sates Environmental Protection Agency. Integrated Risk Information System. Benzene (CASRN 71-43-2), Washington (DC); 2003 [cited 2013 May 16]. Available from: http://www.http://www.epa.gov/iris/subst/0276.htm

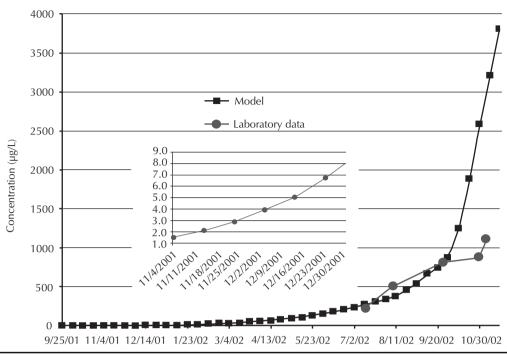


Figure 2. Benzene in water from shallow well 1- data obtained in the laboratory and estimated by the MODFLOW inverse model. Federal District, Brazil.

**Table 2.** Benzene exposure through different pathways and associated non-cancer and cancer risks as a consequence of the fuel leak. Federal District, Brazil.

Estimate -	Age group (years)									
Estimate	< 1	1 a 11	12 a 17	≥ 18 M	≥ 18 W					
Oral exposure - Slope factor: 5.5 x 10-5per μg/kg bw/day; RfD: 4 μg/kg bw day <sup>b</sup>										
OE <sub>w</sub> <sup>a</sup> , μg/kg bw/day	0	0.0080	0.0076	0.0080	0.0090					
OE <sub>,</sub> , μg/kg bw/day	0	0.0002	0.0001	0.0001	0.0001					
TEoral, μg/kg bw/day	0	0.0082	0.0077	0.0081	0.0091					
% RfD	0	0.20	0.19	0.20	0.23					
Cancer risk, per 106 inhab.	0	4.4 x 10 <sup>-7</sup>	4.2 x 10 <sup>-7</sup>	4.5 x 10 <sup>-7</sup>	5.0 x 10 <sup>-7</sup>					
Drinking water risk level <sup>a,b</sup>	0	1 per 10 <sup>4</sup>								
Dermal exposure										
DE <sub>w</sub> , μg/kg bw/day	0.0117	0.0130	0.0061	0.0056	0.0125					
1% absorbed, μg/kg bw/day	1.2 x 10 <sup>-4</sup>	1.3 x 10 <sup>-4</sup>	6.1 x 10 <sup>-5</sup>	5.6 x 10 <sup>-5</sup>	1.2 x 10 <sup>-4</sup>					
% RfD	0.0029	0.0032	0.0015	0.0014	0.0031					
Cancer risk, per 106 inhab.	1.6 x 10 <sup>-7</sup>	1.8 x 10 <sup>-7</sup>	8.3 x 10 <sup>-8</sup>	7.7 x 10 <sup>-8</sup>	1.7 x 10 <sup>-7</sup>					
Inhalation exposure - Unit risk: 7.8 x 10-6μg/m³; RfC: 30 μg/m³ b										
$C_{air'} \mu g/m^3$	7.5	7.5	3.7	3.7	3.7					
% RfC	25	25	12.3	12.3	12.3					
Cancer risk, per 106 inhab.	1.8	1.8	1.8	1.8	1.8					
Air risk level <sup>b</sup>	1 per 10 <sup>5</sup> to 1 per 10 <sup>4</sup>		1 per 10 <sup>5</sup>	1 <i>per</i> 10⁵	1 per 10 <sup>5</sup>					
Total cancer risk, per 106	110-	200	110	110	110					

 $OE_w$ : dose of exposure from water consumption;  $OE_i$ : dose of exposure from food consumption;  $TE_{oral}$ : total oral dose of exposure;  $C_{air}$ : average concentration of benzene in air while showering, RfD: benzene chronic reference dose; RfC: benzene chronic reference concentration;  $DE_w$ : dermal dose of exposure; M: men; W: women

<sup>&</sup>lt;sup>a</sup> At 104.2 µg/L <sup>b</sup> IRIS – Integrated Risk Information System. Benzene (CASRN 71-43-2), Washington (DC): U.S. Environmental Protection Agency, 2003. Available from: http://www.epa.gov

they remained in contact with contaminated water. There is no reference dose or a quantitative estimate of carcinogenic risk for dermal exposure to benzene. As dermal absorption of benzene is about 1% of the applied dose, the non-cancer and cancer risks from dermal exposure to benzene were estimated considering that 1% of the DEw was absorbed. The dermal exposure represented a maximum of 0.0032% of the oral RfD, with a maximum cancer risk of 1.8 x 10<sup>-7</sup>per 10<sup>6</sup> inhabitants (Table 2).

The mean benzene concentrations in the air while showering (3.7 to 7.5  $\mu$ g/m³) represented a maximum of 25% of its chronic inhalation reference concentration (RfC: 30  $\mu$ g/m³) (Table 2). The cancer risk ranged from 1 per 10⁵ to 1 per 10⁴ inhabitants for children > 11 years (air benzene concentration between 1.3 to 4.5  $\mu$ g/m³ represents a risk level of 1 per 10⁵ inhabitants).

The total cancer risk from benzene from all exposure pathways ranged from 110 (adolescents and adults) to 200 (children under 12) per 10<sup>6</sup>, mainly due to the consumption of water and inhalation while showering (Table 2). Cancer risks from dermal water contact and fruit consumption were negligible. These levels are higher than those found by López et al<sup>13</sup> (<2.9 x 10<sup>-10</sup> per 10<sup>6</sup> for children) for a Spanish population living near an area where an oil leak occurred, with dermal exposure contributing to <0.1% of the total risk.

The Fuel Distributer assessed the risk of the affected community from exposure to BTEX using the RBCA Tier 2 Reverse Mode. The site-specific target level for benzene in the ground water, above which there is a risk to human health (ASTM-1739/95), was estimated to be 9.9 µg/L. The Reverse Model estimated that the water consumed by the community had benzene level at 17.2 µg/L, lower than the level estimated in this study. The indoor and outdoor benzene levels in the air were estimated to be 1.8 and 640 µg/m<sup>3</sup>, respectively. Only inhalation of water vapor during shower was considered in the present study, as it is the main source of indoor air exposure. 12 Outdoor air benzene concentration was not estimated by the inverse model. The outdoor exposure to benzene through inhalation can be estimated using the outdoor benzene level estimated by the Distributer, the ATSDR methodology<sup>f</sup> and the exposure factors recently estimated by the USEPA (inhalation rates and maximum exposure times). b The exposure levels ranged from 0.9 to  $2.0 \mu g/kg$  bw/day (for children < 12), higher than the TE<sub>oral</sub>, potentially increasing the total cancer risk estimated previously.

The mathematical contour conditions of the RBCA methodology used by the fuel distributer to estimate the benzene concentration in water assumes constant concentration and permanent flow, with transport by advection and dispersion. The model used in this study adds cosolvency effect to the transport and decay and

retardation of the contaminant, considering a heterogeneous, anisotropic and transient flow aquifer. The velocity distribution of groundwater flow was shown to be a major factor influencing the shape and migration velocity of the contaminant due to a system of geological faults identified and incorporated into the model.

Biochemical blood exams were performed on the affected community on several occasions between May, 2002 and September, 2004, with an average of five exams per person. Out of the 31 parameters investigated in each exam, seven showed alterations: four related to the red blood cells (mycrocytosis, macrocytosis, decrease and increase of the mean corpuscular hemoglobin – MCH), one related to white blood cells (lymphocytopenia) and two related to the liver function (increased levels of alanine and aspartate aminotransferases). Lower MCH and lymphocytopenia were the most prevalent alterations. Six individuals fit the suspicion protocol (alterations in at least two consecutive tests over 60 days): five adult women (up to six alterations), and the 6-month-old male baby (five alterations). Women have significantly higher risk for effects of benzene exposure than men due to factors such as blood/air partition coefficient, higher metabolism rate and body fat.2 Children have greater body surface by weight (nearly three times more than adults), greater respiratory frequency per minute (65 times more than adults), and greater water and food consumption by body weight (more than two times that of adults), a being also a population that should be given special consideration in exposure studies.

The biochemical blood alterations in the affected community have been observed in individuals chronically exposed to benzene in occupational settings. Duarte-Davidson et al, however, concluded, based on human studies, that risk of leukemia or any other adverse health effect in the general population, infants and children at concentrations of exposure of 3.7-42 µg/m³ is likely to be small and probably not detectable with current methods.

This study has many limitations, mainly related to the contaminant data used in the estimation of the doses of exposure through the different pathways. The risk assessment models used contain numerous uncertainties that are typically compensated for by conservative assumptions that lead to an overestimation of the risks. The models used health parameters (RfD and cancer risk) for a chronic lifetime exposure, while the community evaluated in this study was exposed to benzene for < 7 months. Although urine analysis for biomarker of exposure to benzene (*trans-trans* muconic acid) was conducted in the affected population in September 2002, they were considered unreliable as they all gave negative results. Background levels of *trans-trans* muconic acid in the Brazilian general population ranges from 3 to 555 μg/g

creatinine,<sup>7</sup> similar to what has been reported for non-smokers elsewhere.<sup>1,3</sup> The residential area is confined with a highway (Figure 1), and at least the benzene exposure deriving from traffic should have been detected.

# **CONCLUSIONS**

The exposure to benzene after a gasoline station fuel leak may have caused adverse health effects in the population who used and consumed contaminated water. A high risk perception was evident within the community, probably due to the lack of assistance from government authorities and the polluting agent, which generated insecurity and mistrust.

Assessments of health effects due to environmental exposure to hydrocarbons and other contaminants are

still incipient in Brazil, mainly due to the lack of appropriate data and trained personal. It is essential that local Brazilian authorities develop better strategies to rapidly respond to fuel leaks in order to protect the health of the affected population and the environment. Both health and environmental authorities need to establish a strong inter-institutional collaboration interface for conducting sound risk assessment studies.

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#### REFERENCES

- Aprea C, Sciarra G, Bozzi N, Pagliantini M, Perico A, Bavazzano P, et al. Reference values of urinary trans, trans-muconic acid: Italian Multicentric Study. Arch Environ Contam Toxicol. 2008;55(2):329-40. DOI: http://dx.doi.org/10.1007/s00244-007-9119-9
- Brown EA, Shelley ML, Fisher JW. A pharmacokinetic study of occupational, and environmental benzene exposure with regard to gender. *Risk Anal*. 1998;18(2):205-13. DOI: http://dx.doi.org/10.1111/j.1539-6924.1998.tb00932.x
- Chakroun R, Faidi F, Hedhili A, Kolsi M, Fehri S, Nouaigui H. Determination of urinary trans, transmuconic acid reference values in general Tunisian population. *Ann Biol Clin (Paris)*. 2009;67(2):163-9.
- 4. Chen Z, Huang GH, Chakma A. Risk assessment of a petroleum-contaminated site through a multiphase and multi-component modeling approach. *J Petrol Sci Eng.* 2000;26(1-4):273-81. DOI: http://dx.doi.org/10.1016/S0920-4105(00)00041-3
- Corseuil HX, Fernandes M. Effect of ethanol in increasing the solubility of aromatic compounds present in Brazilian gasoline. Rev Bras Eng San Amb. 1999;4:71-5.
- Corseuil HX, Kaipper BIA, Fernandes M. Cosolvency effect in subsurface systems contaminated with petroleum hydrocarbons and ethanol. Water Res. 2004;38(6):1449-56. DOI: http://dx.doi.org/10.1016/j.watres.2003.12.015
- de Paula FC, Silveira JN, Junqueira RG, Leite EM. Assessment of urinary trans, trans-muconic acid as a biomarker of exposure to benzene. Rev Saude Publica. 2003;37(6):780-5. DOI: http://dx.doi.org/10.1590/S0034-89102003000600014
- 8. Duarte-Davidson R, Courage C, Rushton L, Levy L. Benzene in the environment: an assessment of the potential risks to the health of the population. *Occup Environ Med*. 2001;58(1):2-13. DOI:http://dx.doi.org/10.1136/oem.58.1.2
- Forte EJ, Azevedo MS, Oliveira RC, Almeida R. Hydrocarbon contamination in groundwater: the case of Tupi Village, Porto Velho-RO. Quim Nova. 2007;30(7):1539-44. DOI: http://dx.doi.org/10.1590/S0100-40422007000700008
- Galbraith D, Gross SA, Paustenbach D. Benzene and human health: a historical review and appraisal of associations with various diseases. *Crit Rev Toxicol*. 2010;40(Suppl 2):1-46.

- 11. Jamall IS, Willhite CC. Is benzene exposure from gasoline carcinogenic? *J Environ Monit*. 2008;10(2):176-87. DOI:http://dx.doi.org/10.1039/b712987d
- 12. Lindstrom AB, Highsmith VR, Buckley TJ, Pate WJ, Michael LC. Gasoline-contaminated ground water as a source of residential benzene exposure: a case study. *J Expo Anal Environ Epidemiol*. 1994;4(2):183-95.
- López E, Schuhmacher M, Domingo JL. Human health risk of petroleum-contaminated groundwater. *Environ Sci Pollut Res Int*. 2008;15(3):278-88. DOI:http://dx.doi.org/10.1065/espr2007.02.390
- National Research Council. Alternatives for ground water cleanup: Washington (DC): National Academies Press; 1994
- Powers SE, Hunt CS, Heermann SE, Corseuil HX, Rice D, Alvarez PJJ. The transport and fate of ethanol, and BTEX in ground water contaminated by gasohol. Critical Rev Environ Sci Technol. 2001;31(1):79-123. DOI:http://dx.doi.org/10.1080/20016491089181
- Rabiee F. Focus-group interview and data analysis. *Proc Nutr Soc.* 2004;63(4):655-60. DOI:http://dx.doi.org/10.1079/PNS2004399
- Rego ECP, Pereira Netto AD. PAHs, and BTEX in ground water of gasoline stations from Rio de Janeiro city, Brazil. *Bull Environ Contam Toxicol*. 2007:79(6):660-4. DOI: http://dx.doi.org/10.1007/s00128-007-9300-x
- 18. Silva RL, Barra CM, Monteiro TCN, Brilhante OM. Estudo da contaminação de poços rasos por combustíveis orgânicos e possíveis consequências para a saúde pública no Município de Itaguaí, Rio de Janeiro, Brasil. Cad Saude Publica. 2002;18(6):1599-607. DOI: http://dx.doi.org/10.1590/ S0102-311X2002000600014
- Tiburtius ERL, Zamora PP, Leal ES. Contaminação de águas por BTXs e processos utilizados na remediação de sítios contaminados. Quim Nova. 2004;27(3):441-6. DOI: http://dx.doi.org/10.1590/S0100-40422004000300014
- Vinci RM, Jacxsens L, Loco J, Matsiko E, Lachat C, Schaetzen T, et al. Assessment of human exposure to benzene through foods from the Belgian market. *Chemosphere*. 2012;88(8):1001-7. DOI: http://dx.doi.org/10.1016/j.chemosphere.2012.03.044