



National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

**Risk assessment of an increased
concentration limit of benzene in
natural gas**

RIVM Letter report 601352002/2013
P.C.E. van Kesteren et al.



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Colophon

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Rapport in het kort

Gezondheidsrisico bij verhoging benzeenlimiet in aardgas niet waarschijnlijk

Benzeen is een vluchtige vloeistof die kankerverwekkend is. Om te voorkomen dat het risico's voor de gezondheid vormt, is het gebruik van benzeen wettelijk beperkt. Voor de huidige Europese stoffenwetgeving REACH wordt de maximaal toegestane aanwezigheid van benzeen in aardgas aangegeven als een gewichtspercentage (0,1 procent overeenkomend met 1 g benzeen per 1000 g aardgas). Er bestaan plannen om deze duiding gelijk te trekken met de duiding voor gassen in andere wettelijke kaders. Daarin wordt de maximale hoeveelheid als een volumepercentage aangegeven (0,1 procent overeenkomend met 1 liter benzeen per 1000 liter aardgas).

Volgens het RIVM is het onwaarschijnlijk dat deze omzetting gezondheidsrisico's kan veroorzaken bij reguliere situaties waarin mensen via aardgas blootstaan aan benzeen. Dit geldt bijvoorbeeld voor consumenten thuis bij het gebruik van aardgas in de keuken, of voor werknemers die werkzaamheden uitvoeren bij gasleidingen, meetstations en dergelijke. In deze situaties blijft de blootstelling aan benzeen onder de grenswaarde.

Voor enkele situaties is het niet bekend of er gezondheidsrisico's ontstaan. Volgens de huidige gegevens zou er een risico voor de gezondheid kunnen ontstaan bij kleine lekkages van aardgas in huis die niet worden opgemerkt, of bij industrieel gebruik, zoals onderhoudswerkzaamheden. Dit geldt echter zowel voor de huidige limiet als voor de 'nieuwe' limiet op basis van volume. Er zit echter veel onzekerheid in de geschatte blootstellingsniveaus en de kans dat zulke blootstellingssituaties zich voordoen is klein. Meer informatie is nodig over de daadwerkelijke blootstelling bij dergelijke situaties om een realistischere schatting te kunnen maken.

Trefwoorden: benzeen, aardgas, REACH, restrictie, blootstelling, massafractie, volumeprocent

Abstract

Health risks due to an increased limit for benzene in natural gas are unlikely

Benzene is a volatile liquid that is carcinogenic. To prevent risks for human health the use of benzene is restricted. Within the current European substances regulation REACH the presence of benzene in natural gas is indicated as mass fraction (0.1 percent comparable with 1 g benzene in 1000 g natural gas). It is proposed to change this to the same indication as set for gases in other European legal frameworks. In those other frameworks maximum levels are indicated as volume fraction (0.1 percent comparable with 1 litre benzene in 1000 litres natural gas).

According to the RIVM it is unlikely that this conversion causes health hazards in regular situations of human exposure to benzene via natural gas. This applies to the use of natural gas at home in the kitchen, for workers that carry out maintenance work at gas stations etcetera. In such situations the exposure to benzene remains below the safety limit.

In some situations it is unknown if risks for human health may arise. According to the current information the exposure to benzene may be too high in case of small leaks of natural gas in homes that are not noticed or during industrial uses, such as maintenance work. However, this applies both to the current limit as to the limit based on the volume fraction. Further, there is a lot of uncertainty in the estimations of exposure levels and the likelihood that such exposure situations occur is very small. More information about the actual exposure levels is required in order to make a more realistic estimate.

Keywords: benzene, natural gas, REACH, restriction, exposure, mass fraction, volume fraction

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Summary

Benzene is a mutagenic and carcinogenic substance which use is currently restricted to 0.1% w/w as a constituent of other substances or in mixtures, according to the REACH Annex XVII (Entry 5) legislation. It is proposed to adjust this restriction to other European legislations for gases by changing the limit to 0.1% v/v benzene for gasses. We evaluated if this change to volume percentage can result in an unacceptable risk for humans. The evaluation was limited to exposure to benzene via natural gas, from which the highest exposure levels can be expected, resulting in an approximately four times higher allowed benzene concentration. Several scenarios for consumer exposure, occupational exposure and exposure via the environment were identified and corresponding exposure levels associated with 0.1% w/w and 0.1% v/v benzene in natural gas were estimated. Comparison of most exposure estimates with existing exposure limits for consumers and workers showed that the use of 0.1% v/v benzene in natural gas will not lead to an unacceptable risk for humans during regular exposures to natural gas. Although considered unlikely, exposures of consumers in case of a small gas leak may exceed the corresponding limit value. Exposure levels of workers during industrial use may exceed the occupational limit values in most identified scenarios, as the measures to limit the risk of explosion are not protective against the risk of exposure to benzene. The estimated exposures levels of humans exposed via the environment showed no unacceptable risk at 0.1% v/v benzene in natural gas. In all cases (consumers and industrial) where limit values were exceeded, it applied to both 0.1% w/w and 0.1% v/v benzene in natural gas. However, due to the limited information provided for these scenarios it remains unclear how realistic the exposure levels are. Therefore, it is concluded that an unacceptable risk due to a change in benzene restriction cannot be excluded. More information on the actual exposures is required for these scenarios to create realistic risk estimations. It is noted that it remains unclear whether benzene exposure during professional and industrial use is covered by the exception in REACH Annex XVII for certain industrial processes.

1 Introduction

1.1 Restriction of benzene use

Benzene is a volatile liquid that exists as a natural constituent in crude oil and natural gas. Benzene is mainly used in the chemical industry for the synthesis of other chemicals and it is present as a constituent in motor fuels and natural gas. The use of benzene is restricted; according to Annex XVII (Entry 5) of the REACH legislation (EC, 2006a) benzene shall not be used or placed on the market as a substance or as a constituent of other substances, or in mixtures, in concentrations $\geq 0.1\%$ by weight (w/w). This restriction does not apply to motor fuels, which are covered by Directive 98/70/EC (EC, 1998) and to 'substances and mixtures for use in industrial processes not allowing for the emission of benzene in quantities in excess of those laid down in existing legislation'. The weight-based restriction for benzene is being discussed, since most other European legislations concerning gases (EC, 1999a; EC, 2008a) are based on volume percentages. A change from weight percentage to volume percentage for gases will result in 4.2x higher maximum allowable benzene concentration (w/w), as calculated based on the ideal gas law (see Appendix 2 and 4 for calculations). Therefore, an evaluation of the consequences for human risk assessment is required.

1.2 Natural gas: from extraction to use

The highest volumes of gas containing benzene are registered for natural gas. Most benzene concentrations in natural gas are below the limit of 0.1% w/w. Occasionally, benzene concentrations (in natural gas from small fields) exceed the limit with concentrations up to 0.42 % w/w (see Appendix 1). Therefore, exposure to benzene via natural gas was selected for evaluation. Natural gas is defined as raw natural gas, as found in nature, or a gaseous combination of hydrocarbons having carbon numbers predominantly in the range of C1 through C4 separated from raw natural gas by the removal of natural gas condensate, natural gas liquid, and natural gas condensate/natural gas (EPA, 2013). The composition of distributed 'Groningen' natural gas, used as a reference, consists of 81.3% v/v methane, 14.4% v/v nitrogen, 2.9% v/v ethane and 1% v/v other gases (GTS, 1988).

Natural gas is extracted from multiple sources at sea and on land. The extracted gas is purified and separated from fluids such as natural gas condensate and water to form dry gas. Extracted dried gas is collected at entry points and entered into the main gas grid of the Dutch Gas Transport Services (GTS). The main gas grid consists of a high pressure grid and a low pressure grid. In the high pressure grid the pressure is maintained by compressor stations at maximum 67 or 80 bar overpressure to facilitate the transport. The low pressure grid has a maximum overpressure of 40 bar.

The gas from the high pressure grid is transported a) directly to industrial users or local distribution companies via gas delivery stations, or b) to the low pressure grid via a measuring and regulation station. The amount of gas and the gas quality are measured and the pressure is reduced to the desired pressure of the industrial user or to the pressure level of the low pressure grid (40 bar). In the gas receiving stations or at the measuring and regulation stations the gas may be odorized with tetrahydrothiophene (THT) to enable the detection of leaks. From the measuring and regulation stations the gas is then transported

via the low pressure grid to gas delivery stations, where the low pressure grid is connected to the local distribution grid (owned by local distribution companies) and industry as well. The gas delivered to local distribution companies is always odorized with THT.

The gas quality in the GTS gas grids is controlled in blending stations. Natural gas has different compositions depending on its source, which affect the amount of energy released during combustion, referred to as calorific value. In principle, two grid quality grids can be identified:

1. high-calorific gas grid (H-gas)
2. low calorific gas grid (G-gas)

H-gas is delivered to industry or users via two routes. Following the first route the gas is blended with other H-gas and delivered to typically industrial users. In the second route, G-gas is injected with nitrogen and/or the gas stream is blended with low-calorific gas at blending stations, thereby delivering a constant G-gas quality of natural gas to industrial users and consumers.

Gas for consumer use is distributed mainly to households where the pressure is reduced from 4 or 8 bar overpressure to 25 mbar overpressure, so the gas can be used by domestic or small commercial consumers (NEN-EN 437, 2009; personal communication NOGEPA and GTS).

The high calorific grid transports the high calorific gas containing the highest amount of benzene, while the low calorific grid transports low calorific gas (G-gas or the so called pseudo G-gas). G-gas or 'Groningen' gas contains only very small amounts of benzene (0.075 % w/w). If insufficient Groningen gas is available GTS makes pseudo G-gas by blending high calorific gas with approximately 14% nitrogen.

As described above, natural gas which is supplied to the local distribution grid network is odorized, making it possible to detect natural gas by smell. However, end users directly connected to the main transport network may demand not to odorize the gas. In those situations extra safety precautions have to be taken, such as marking of the area where the gas is used and the use of gas detection equipment. In such cases, gas detection depends on the equipment, which gives an alarm at 10% of the lower explosion limit (LEL). Since the LEL is reached at 5% natural gas in air, the alarm will be given at 0.5% v/v natural gas in air.

1.3 Odorization of natural gas

Natural gas is odorized to make detection possible. According to the Dutch standard NEN 7244-1 (2009), distributed natural gas shall have a recognizable and alarming smell when 20% of the LEL of natural gas in air is reached, resulting in a limit for detection of 1% natural gas in air.

The THT concentration that 50% of humans can smell, defined as odour threshold, is 1 ppb, corresponding to $3 \mu\text{g}/\text{m}^3$ (Otte et al., 2007). According to the Dutch connection and transport conditions (NMA, 2011), natural gas supplied to the regional distribution network operators shall be odorized with minimally $10 \text{ mg}/\text{m}^3$ THT. Currently, a concentration of $18 \text{ mg}/\text{m}^3$ THT is injected to guarantee the level of $10 \text{ mg}/\text{m}^3$ at all exits (personal communication GTS). Considering the limit of $10 \text{ mg}/\text{m}^3$ THT, the percentage natural gas in air that 50% of the people can smell is maximally 0.03% ($3 \mu\text{g}/\text{m}^3 / 10,000 \mu\text{g}/\text{m}^3 \times 100\%$), showing that natural gas can be smelled at an approximately four times lower concentration compared to the limit of 1% gas in air.

1.4 Other gases

The proposed change of the benzene restriction also affects other gases besides natural gas. A limited search was performed to identify other gases that contain or could contain benzene. Annex VI of CLP was scanned for entries containing the word benzene or containing a note J and assessed whether they were gases or not. In note J (CLP Annex VI chapter 1.1.3.1) it is described that the classification as a carcinogen or mutagen does not need to be applied if it can be shown that the substance contains less than 0.1% w/w benzene (EINECS No 200-753-7). This note applies only to certain complex coal- and oil-derived substances. Only certain types of refinery gas were identified as gases containing or possibly containing benzene. In agreement with the commissioning organization (Ministry of I&M) an assessment of the effect of the proposed change of the restriction for this group of gases was however not performed, as this was limited to natural gas.

1.5 Exposure scenarios

The restriction for benzene as described in the current version of Annex XVII accounts for placing benzene on the market and for use of benzene (EC, 2006a). The manufacturing of natural gas, including extraction and purification, is excluded. In the case of natural gas, the restriction is therefore applicable starting at the entry point to the main network until the endpoints where the gas is actually used. This includes blending stations and measuring and regulation stations where gas is measured or blended. Possible exposures to natural gas can occur during use in industries, maintenance work, gas sampling, and actual use of the gas such as refuelling or cooking.

The REACH legislation does not apply to the transport of substances, with the exemption of repair and maintenance work. According to the legislation, transport is defined as the carriage of dangerous substances and dangerous substances in dangerous preparations by rail, road, inland waterway, sea or air (EC, 2006b). In agreement with the commissioning organization (Ministry I&M) it was decided that this definition does also account for transport through pipelines. Transport through pipelines is therefore not included in this assessment.

The REACH legislation (Annex VII, entry 5) covers the use and placing on the market of benzene, however an exception is made for 'substances and mixtures for use in industrial processes not allowing for the emission of benzene in quantities in excess of those laid down in existing legislation'. Since it is uncertain whether the exposure scenarios for professional and industrial use are covered by the exception in REACH, these were included in our assessment.

1.6 Aim

The aim of this report is to determine if the change of a concentration from 0.1% w/w to 0.1% v/v benzene in natural gas can result in an unacceptable risk for humans. Several exposure scenarios were identified for workers and consumers and exposures were estimated and compared to human exposure safety limits. A risk was defined as unacceptable if the corresponding human safety limit was exceeded.

2 Hazard identification and human exposure limits

2.1 Hazard identification

The toxicokinetics and toxicity of benzene have been extensively studied in organisms and humans. An overview is given in the Risk Assessment Report (RAR) reported by Germany (EC, 2008b) and is summarized here.

Benzene can be absorbed via inhalation, dermal exposure and oral exposure, with inhalation as the most important route of exposure. Benzene is rapidly distributed in the body and is mainly found in lipid-rich tissues. Most of the benzene is metabolized by cytochrome P450 enzymes, mainly in the liver, and excreted via urine. Oxidative metabolism is required for manifestation of toxic effects of benzene.

Benzene is irritating to skin, eyes and respiratory tract and can cause chemical burns, collapse, haemorrhagic lungs, pulmonary oedema, bronchitis and pneumonia by acute dermal or inhalation exposure. It was documented that in humans, an inhalation exposure to 0.16-0.48 g/m³ for 6 hours can result in headache and lassitude, while 0.08 g/m³ gave no acute effects. The main targets after repeated exposure are cells of the haematopoietic system (i.e. bone marrow, spleen, thymus, lymph nodes). Chronic exposure can result in bone marrow depression, anaemia and thrombocytopenia. Benzene has a harmonized classification as mutagenic (CLP 1B) and carcinogenic (CLP 1A). Benzene is predominantly a clastogen in mammals, especially chromosomal aberrations and micronuclei are induced. Carcinogenicity was shown in inhalation studies with mice and rats with tumours predominant in the haematopoietic system, particularly lymphomas in mice and leukaemia in rats. Human epidemiological data have shown a causal relationship between benzene exposure and acute and chronic leukaemia. Evidence from human and animal data is not sufficient to demonstrate a relationship between benzene exposure and impairment of the reproduction system.

According to the RAR (EC, 2008b), the mutagenicity and carcinogenicity of benzene are the only concerns for risk characterization of prolonged exposure to benzene, for both workers and consumers. Current exposure limits are based on the carcinogenic and mutagenic potential of benzene. In agreement with the RAR, risk assessments in this report were also limited to the mutagenic and carcinogenic potential of benzene.

2.2 Exposure limits workers

Benzene is a genotoxic carcinogen and therefore no safe level of exposure can be recommended. Risk assessment is generally performed with non-threshold linear extrapolation models to estimate the risk associated with low exposure levels.

For non-threshold substances, REACH requires to set, where possible, derived minimal effect levels (DMELs). A DMEL corresponds to a level of very low concern and is derived for both workers and consumers. According to the REACH guidance, cancer risk levels of 10⁻⁵ and 10⁻⁶ can be seen as indicative tolerable risk levels for workers and the general population respectively (REACH guidance part E: Risk Assessment). So far, one registrant has derived a DMEL for benzene, which is 3.2 mg/m³ for acute and long term exposure via inhalation. All other registration dossiers do not contain DMELs, because of registration as intermediate used in a closed system.

Under worker protection legislation, a binding occupational exposure limit (BOEL) for benzene is in place of 1 ppm (3.25 mg/m³) 8 hours time-weighted average (TWA) (SER, 2013). This limit was set by the SCOEL (EC, 1992). The limit is based on a study by Rinsky *et al.* (1981, 1987), who conducted a retrospective cohort mortality study of workers who had been exposed to benzene during the manufacturing of Pliofilm (further referred to as Pliofilm cohort). These cohort data were further used to estimate the risk of benzene exposure, resulting in a range of 0.5-6.6 additional leukaemia cases per 1000 workers exposed to 1 ppm benzene over a working lifetime of 40 years (Rinsky *et al.*, 1987; Crump and Allen, 1984; Brett *et al.* 1989). In addition, the RAR (EC, 2008b) reported a possible range of 0.02-0.036 cases per 1000 workers for an average exposure of 1 ppm over 45 years, based on analysis of the Pliofilm cohort by Crump (1994).

The current OEL for benzene in most European countries, including the Netherlands, is 1 ppm. However, in Sweden, Denmark and Switzerland the current limit value is 0.5 ppm (8 hour TWA) (SER, 2013).

In this report, the risk for workers is considered unacceptable when the OEL value of 3.25 mg/m³ (1 ppm) is exceeded.

2.3 Exposure air quality limits consumers

The current European air quality limit value for benzene is 5 µg/m³, corresponding to an additional cancer risk of 1 in a million per lifetime (EC, 2000; EC, 2008b). This limit value is based on World Health Organization estimations (WHO, 2000) and on a meta-analysis of Wong and Raabe (1995). The WHO determined a limit value of 0.17 µg/m³ (cancer risk of 10⁻⁶ in a lifetime) based on multiplicative risk estimates with the Pliofilm cohort data by Crump (1994), who estimated an excess lifetime risk of leukaemia of 6 x 10⁻⁶ at a concentration of 1 µg/m³. To cover more recent occupational studies, the meta-analysis of Wong and Raabe (1995) that revealed a risk in the order of 5 x 10⁻⁸ was also taken into consideration. Based on both analyses, the EC has defined a limit range of 0.2-20 µg/m³ benzene associated with an excess risk of leukaemia of 1 in a million (EC, 1999b). A limit value of 5 µg/m³, with an averaging measuring period of one year, was determined to be protective and feasible (EC, 2008c). The current (non-legally binding) target limit in the Netherlands, as determined by the Dutch Ministry of Infrastructure and Environment, is 1 µg/m³ (de Jong and Janssen, 2011).

In this report, the risk for consumers is considered unacceptable when the limit value of 5 µg/m³ is exceeded, since this limit is legally bound.

3 Exposure of consumers

Plausible (non-industrial) consumer exposure scenarios were described and for those considered relevant for the present risk assessment exposure estimates were generated. These estimates are made for 0.1% w/w and 0.1% v/v benzene in natural gas.

3.1 Routes and use leading to exposure

Exposure of a consumer to natural gas is due to the regular use of a natural gas as fuel for cooking and heating and as fuel for transportation. Additionally unintended exposure may occur due to gas leaks. We identified the following consumer exposures to natural gas, which are exposure:

- 1) as a result of cooking
- 2) as a result of heating
- 3) as a result of small gas leaks without smelling the tracer THT
- 4) as a result of refuelling private cars using natural gas.

3.2 Exposure scenarios for consumers

3.2.1 *Exposure due to cooking*

In the Netherlands many households use natural gas for cooking. During cooking with natural gas the consumer can be exposed to benzene in the gas. The exposure will occur because unburned gas is released into the kitchen during the few seconds from when the gas tap is opened until ignition of the gas. Once the gas is burning, benzene is also burned and the consumer is no longer exposed.

- What happens when the flame suddenly dies?
Natural gas is highly flammable and explosive and therefore, when released without controlled burning, very dangerous. Because of its nature, gas cooking rings nowadays all have a thermal safety device. This thermal safety assures that, when the flame dies, the gas is automatically turned off. Since April 2010 all cooking rings sold, must include a thermal safety. Old cooking rings may not have such a thermal safety and when the flame dies large amounts of unburned gas may be released into the kitchen. Although such a natural gas release may occasionally occur, the risks of acute poisoning by natural gas or gas explosions, considerably outweighs the acute and long-term risk of exposure to benzene. Additionally, THT will warn the consumer that gas is leaking, which will trigger action. This situation is considered as accidental and therefore outside the scope of the present evaluation.
- How long is gas released into the kitchen during cooking?
In the Netherlands two types of gas cooking rings are used: cooking rings with or without electronic ignition. The former ones are nowadays used predominantly. According to information from ATAG (personal communication), rings with electronic ignition are controlled in such a way that every second a spark is generated which can ignite the gas. Generally, within a few seconds the gas will ignite. Modern cooking rings of ATAG can generate maximally 10 sparks. After ten sparks the gas is turned off automatically. Most of the times the flame burns after the third spark, thus after 3 seconds. Cooking rings without electronic ignition need to be ignited by the consumer by hand, for instance using matches or candle lighters. With this type of cooking

ring the period of the gas released into the kitchen depends on how fast the consumer lights the flame. Assuming a consumer first turns on the gas, then picks-up and strikes a match and subsequently lights the flame, the release of gas into the kitchen will probably be longer as compared to the 3 seconds when using the cooking ring with electronically ignition. A period of 3 to 5 seconds may not be uncommon. Longer periods are considered not likely, since ignition will then cause a burst of flame, which consumers will try to avoid. Assuming that it takes 5 seconds before the flame burns, it seems reasonable to assume that not all the gas released during this period has been burned.

- How much gas is released per second?

The amount of energy obtained from Dutch natural gas is 31.66 MJ/m³, or 8.82 kWh/m³ natural gas (GTS, 1988). The capacity of Dutch standard gas cooking ring¹ varies from 1.5 to 5 kWh (websites Siemens, ATAG, Bosch). During ignition, the supply of gas ring needs to be low otherwise the gas will not ignite. According to information of Siemens (personal communication) the capacity of a gas ring with the gas supply turned low is a tenth of the maximum, thus the capacity during the ignition phase is 0.15 to 0.5 kWh. During ignition, a gas ring with a low gas supply will release 4.72×10^{-6} to 1.57×10^{-5} m³ natural gas per second.

Scenario cooking exposure

A consumer cooks daily on a natural gas cooker/stove, without electronic ignition. It is assumed that the stove ring has two cooking rings with an ignition capacity of 0.15 kWh and two rings with an ignition capacity of 0.5 kWh. The four rings are assumed to be used simultaneously for preparing dinner. One of the rings with an ignition capacity of 0.5 kWh is assumed to be used additionally 6 times per day boiling water for tea. Assuming the natural gas contains 0.1% v/v or 0.1% w/w benzene the consumer will inhale benzene, which will be instantaneously dispersed throughout the kitchen along with the natural gas. The room volume of the kitchen is assumed to be 15 m³ and the kitchen is ventilated 2.5 times/hour (ConsExpo 4.1). It is assumed that the cooking of the dinner takes 60 minutes and preparing tea will take 15 minutes. Detailed scenario descriptions are provided in Appendix 2.

Exposure estimates

With the ConsExpo inhalation model for instantaneous release and the accompanying Fact Sheets (www.consexpo.nl) the inhalation exposure to benzene (0.1% v/v) in natural gas was calculated for cooking dinner (15 and 60 min) and preparing tea (15 min) (see Appendix 2 and 3).

The inhalation exposure to benzene (0.1% w/w) in natural gas containing was calculated by reducing the calculated 0.1% v/v estimates with a factor 4.2 (see calculation in Appendix 2).

Table 3.1 presents the mean benzene concentrations in the kitchen air during cooking dinner (15 and 60 minutes) and preparing tea (15 minutes). These values will be taken forward to the risk characterization.

Table 3.1. The estimated mean benzene air concentrations in the kitchen, due to natural gas containing 0.1% v/v or 0.1% w/w benzene (see Appendix 2).

Concentration benzene in natural gas	Exposure time	Mean concentration benzene in air ($\mu\text{g}/\text{m}^3$)	
		Cooking	Tea
0.1% v/v	15 min	33.7	12.9
	60 min	16.7	-
0.1% w/w	15 min	8.0	3.1
	60 min	4.0	-

3.2.2 *Exposure due to heating*

In the Netherlands the vast majority of domestic homes are heated with central-heating boilers. The techniques involving this type of heating are well developed. The flame of the central-heating boiler can only be ignited electronically. The burner of the boiler is sealed-off from the outside in such a way that no natural gas can escape. It's therefore concluded that there will be no exposure from central-heated boilers during ignition of the flame and during daily operation of the boiler.

Besides central-heating boilers, domestic homes are sometimes also heated with gas heaters. During the ignition of the flame the consumer may be exposed to gas, but this will generally only occur at the start of season when heating is needed. During the rest of the heating season the heater will burn on the pilot flame and no gas will escape without burning. In case the pilot flame dies, and the gas heater has not got a thermal safety, considerable volumes of natural gas may be released. In such an event, the risks of acute gas poisoning or explosion caused by the natural gas, considerably outweighs the acute risk of exposure to benzene. Additionally, THT will warn the consumer that gas is leaking, which will trigger action. This situation is considered as accidental and therefore outside the scope of the present evaluation.

3.2.3 *Exposure due to small gas leaks*

There are no data of indoor air benzene or natural gas concentration available that are due to natural gas leaks. Therefore it is not possible to estimate exposures from it.

However, in the Netherlands an odour substance (THT) is added to natural gas. This is an explosion safety measure in case of leaks. The THT odour limit of $3 \mu\text{g}/\text{m}^3$ (Otte et al., 2007) is very low and can already be smelled when the concentration of natural gas is still far below the level at which it is flammable or explosive. According to the Dutch connection and transport conditions (NMA, 2011) the minimal THT concentration in natural gas is $10,000 \mu\text{g}/\text{m}^3$. This means that the consumer may detect natural gas containing THT when the concentration of natural gas in air exceeds 0.03 %.

In theory, a consumer can be exposed to natural gas when the THT concentration remains below $3 \mu\text{g}/\text{m}^3$. However, it is very unlikely that the air would contain 0.03 % natural gas due to gas leaks for a prolonged period of time. Gas concentrations will vary between rooms, due to different ventilation rates. Concentrations might accumulate above the odour threshold when ventilation is lacking or can reduce to well below the odour threshold in highly ventilated rooms. The chance that an equilibrium between the gas leakage and ventilation is reached at levels just below the odour threshold is low. However, considering the millions of households in the Netherlands such a situation cannot be excluded. Next to the probability of small gas leaks below the odour

threshold, a consumer will not stay at the exact same location all the time. In addition, a small gas leak is likely to develop into a larger leak over time and will be noticed.

Although it is not clear whether and how often accidental small gas leaks occur and are outside the scope of the present evaluation, the theoretical exposure was calculated to evaluate the possibility of an unacceptable risk. The results are presented below in Table 3.2 (see also Appendix 2).

Table 3.2. Calculated maximum benzene air concentrations due to small leaks of natural gas containing 0.1% v/v or 0.1% w/w benzene (see Appendix 2).

Concentration benzene in natural gas	Mean concentration benzene in air ($\mu\text{g}/\text{m}^3$)
0.1% v/v	1186
0.1% w/w	280

3.2.4 *Exposure during refuelling cars*

In the Netherlands there are 91 refuelling stations for cars using natural gas (NGV-Holland, 2012). On the internet several videos can be found in which the procedure to refuel natural gas is shown (Aardgasauto.com, 2013). During this process the amount of natural gas released into the air is very small. The technique of refuelling with natural gas is completely different compared to the technique used for LPG. LPG is a liquid and natural gas for the car is a compressed gas. The natural gas filling pistol is, in contrast to the LPG filling pistol, a closed system. The dead volume gas of the filling pistol is regained and replaced by air at the end of the procedure (personal communication CNG net). No natural gas is released into the air. We conclude that there will be no consumer exposure during refuelling cars with natural gas.

4 Occupational exposure

In this chapter the exposure to benzene from natural gas is estimated for occupational scenarios. These estimates are made for 0.1% w/w and 0.1% v/v benzene in natural gas.

4.1 Routes and use leading to occupational exposure

Natural gas is transported via pipelines and mainly used in industry and power stations. Because of its explosive character, natural gas is mainly present in closed systems. In REACH legislation, Annex VII entry 5, it is stated that benzene shall not be placed on the market or used. However there is an exception for 'substances and mixtures for use in industrial processes not allowing for the emission of benzene in quantities in excess of those laid down in existing legislation'.

Occupational exposure may occur during professional uses such as:

1. plumbing;
2. professional cooking.

Occupational exposure may occur during industrial uses such as:

1. blow off/venting activities during maintenance and construction;
2. regular maintenance in gas stations
3. sampling and analysis;
4. manufacture of other substances;
5. use in power stations.

The benzene exposure of these professional and industrial uses is calculated since it is uncertain whether they are covered by the exception in REACH.

No occupational exposure measurements are available. Limited information on the operating procedures for some of the scenarios was provided. The data were insufficient for a good description of the scenario. Furthermore, information about the operating procedures cannot be used to estimate benzene exposure since quantitative exposure models are not valid for gases. Therefore, no realistic worst case exposure assessment could be made. However, because of the explosive properties measures are taken to assure that the concentrations in air are clearly below the lower explosive limits.

Therefore, it was calculated whether these measures also result in benzene exposure below the occupational exposure limit (section 4.9).

4.2 Exposure scenarios for plumbers

Based on personal communication, one plausible exposure scenario was identified namely exposure of a plumber during maintenance work in a non-ventilated basement of a residence.

The exposure is estimated based on the release of 5 L gas from the gas pipe the plumber is working on. Considering 0.1% v/v benzene in natural gas, the volume of benzene is 0.005 L. This volume of benzene was calculated to mass by use of the ideal gas law and the molecular weight of benzene, resulting in an

estimated release of 16 mg benzene. The estimated concentration of benzene in a near field of 8 m³ for one hour per working day is 2.0 mg/m³.

Considering 0.1% w/w benzene in natural gas, the volume of 5 L natural gas is equal to 3.9 g of gas and a corresponding amount of benzene of 3.9 mg. The estimated concentration of benzene in a near field of 8 m³ for one hour is 0.49 mg/m³, which is approximately four times below the concentration based on 0.1% v/v.

The estimated exposure time for a plumber to natural gas is one hour per 8-hour working day.

Detailed calculations are provided in Appendix 4.

4.3 Professional cooking

Natural gas is also used for professional cooking for example in restaurants. Estimating the exposure is more difficult than for consumers due to the absence of data on the number of cooking rings, room size and ventilation. Further, a larger variation in these variables is expected. Due to the increased number of cooking rings and higher number of ignitions, a higher release of natural gas and of benzene can be expected. However, the ventilation rate will be much higher to prevent high temperatures and high humidity. This will increase the removal of benzene from the air. Overall, no huge increase in benzene concentration is expected. It is concluded that for consumers there is no unacceptable risk due to cooking. Given the much higher occupational exposure limit of 3.25 mg/m³ compared to the air quality limit of 5 µg/m³ used for consumers (factor 650), it is considered highly unlikely that professional cooking will result in benzene exposure levels above the occupational exposure limit. Therefore, no exposure level for professional cooking is estimated.

4.4 Blow off/venting

During maintenance and construction activities employees of GTS, regional grid operators or contractors sometimes have to depressurize the pipelines or gas receiving stations. To that end, the gas will be blown off in the atmosphere in a controlled way using procedures for blow off. To avoid exposure to natural gas first the dispatchers operate the gas grid in such a way that the pressure in the pipeline or gas receiving station is decreased to values as low as possible. Subsequently the pipeline section is blocked and the gas in this section is transferred into the neighbouring section by using re-compression avoiding emissions. If this re-compression technique cannot be used, GTS will use special vent stacks for the avoidance of exposure of gas to the employees. Since the gas is released at high velocities due to the high pressure, mixing with surrounding air will take place immediately. As a result the natural gas is rapidly diluted in air. No information is available regarding the actual exposure to benzene, but the work procedure involves that the work can be performed safely at 10% LEL, which is 0.5% v/v natural gas (IVM, undated). Therefore, it was checked whether the maximum exposure levels due to protection against explosion were also protective for exposure to benzene. As this comparison is relevant for several scenarios it is provided in a separate sub-chapter (section 4.9).

4.5 Regular maintenance in gas receiving stations

A gas receiving station is constructed in an especially designed building according to amongst others ventilation requirements (measuring and regulation stations are installed in the open air). Employees of GTS who work in gas receiving station in principle can be exposed to natural gas. Therefore, employees always wear gas detection and protective clothes before entering the building. At the moment the gas detection register a gas concentration of 10% LEL the building will be left and the valves are closed to avoid the leakage of more gas. At the moment the concentration of gas is acceptable again the work will be continued. The exposure to gas is in this case very incidental and the duration of exposure is kept very limited.

The work procedure involves that GTS employees can work safely at 10% of the LEL (lower explosion limit) (Gasunie, 2009), which is 0.5% v/v natural gas (IVM, undated). Therefore, it was checked whether the maximum exposure levels due to protection against explosion were also protective for exposure to benzene. As this comparison is relevant for several scenarios it is provided in a separate sub-chapter (section 4.9).

4.6 Sampling

Sampling is performed approximately 130 times per year by various metering employees and laboratory employees. Samples are taken according to the general standard ISO 10715 (1997). Sampling instructions of employees are derived from this standard and refer to 10% LEL as a safe working concentration for natural gas which is 0.5% v/v. Sampling is performed in the open air and minimal emission can occur when a vacuum method is used. No further information was provided to estimate the occupational exposure. Therefore, it was checked whether the maximum exposure levels due to protection against explosion were also protective for exposure to benzene.

4.7 Manufacture of other substances

No information was provided regarding the use of natural gas for the manufacture of other substances. However, it is known that natural gas is used to manufacture methanol. An exposure estimate could not be made due to the absence of information on the exposure scenarios including exposure incidence, duration and level. However, it is reasonable to assume that comparable safety standards apply for this use as for other industrial uses. Therefore, it was checked whether the maximum exposure levels due to protection against explosion were also protective for exposure to benzene.

4.8 Use in power stations

No information was provided regarding the use of natural gas in power stations. An exposure estimate could not be made due to the absence of information on the exposure scenarios including exposure incidence, duration and level. Under normal conditions workers will not be exposed since the gas is in a closed system. However, technicians might be exposed during maintenance and repair, which takes place once per two years per location. It is unknown if the same technicians work at multiple locations and can be exposed repeatedly. It is reasonable to assume that comparable safety standards apply for this use as for other industrial uses. Therefore, it was checked whether the maximum exposure

levels due to protection against explosion were also protective for exposure to benzene.

4.9 Current safety standards

Safety standards to protect workers from the risk of explosion of natural gas apply to several industrial exposure scenarios and are expected to apply to all other industrial exposure scenarios. For several exposure scenarios the provided information was insufficient to make an exposure estimate. However, if it can be shown that the safety standards protecting for explosivity are also protective for the exposure to benzene, than it can be concluded that there is no unacceptable risk for these exposure scenarios.

Standard safety procedures ensure that employees can work safely at 10% v/v of the LEL, which is 0.5% v/v natural gas.

Calculation at a benzene concentration in natural gas of 0.1% v/v

The benzene fraction (0.1% v/v) in 0.5% natural gas is $0.005 * 0.001 = 0.000005\%$. The number of moles of benzene in 1 m^3 gas is 41.48 according to the ideal gas law. This is 3239 g of benzene (molar mass benzene is 78.1). The benzene concentration in 0.5% natural gas is $0.000005 * 3239 \text{ g/m}^3 = 16.2 \text{ mg/m}^3$.

The maximal exposure to benzene when fulfilling the safety standards is thus 16.2 mg/m^3 if the benzene concentration in natural gas is 0.1% v/v.

Calculation at a benzene concentration in natural gas of 0.1% w/w

The amount of natural gas in air (0.5%) is 5 L/m^3 . The mass of natural gas ($M=18.65$) at 20°C is $3.9 \text{ g/m}^3 (= (5 \text{ L} / 24 \text{ L/mol}) * 18.65)$. The benzene concentration (0.1% w/w) in 0.5% natural gas is 3.9 mg/m^3 .

The maximal exposure to benzene when fulfilling the safety standards is thus 3.9 mg/m^3 if the benzene concentration in natural gas is 0.1% w/w.

5 Environmental exposure

Exposure of humans via the environment to benzene can occur directly or indirectly via air, water and soil. Indirect routes are for instance via vegetables and by eating dairy products and meat.

In the EU RAR for benzene (EC, 2008b) the total daily human intake of benzene on the regional (country) scale is estimated to be $3.4 \cdot 10^{-4}$ mg/kg bodyweight per day. The RAR shows that about 97% of the total daily human intake on the regional scale is via inhalation of air. The contribution via drinking water is about 1% and via fish consumption about 2%. The contribution through other routes is negligible (<0.5%).

In the RAR the following conclusion on humans exposed via the environment has been drawn: "Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account". This conclusion is reached because i) there are concerns due to repeated dose toxicity, mutagenicity and carcinogenicity, ii) the predominant indirect exposure of humans via the environment occurs via the air and iii) due to the genotoxic and carcinogenic effects of benzene no safe level of exposure can be recommended.

Because of this conclusion the exposure of humans via the environment focuses on the exposure through the inhalation of air. The focus will be on the contribution of the emission of benzene present in natural gas to the total release of benzene on a country level (the Netherlands) and on the level of the EU.

5.1 Use leading to emission to the environment

Benzene can be released through various applications of natural gas as a fuel. Furthermore, benzene can be released during natural gas transport, distribution, consumption and venting/flaring during natural gas exploration and extraction. Although transport and extraction of natural gas are outside the scope of this project, they are described in this section and used for calculations to get an indication of the total emission to the environment.

Since no detailed benzene emission data are available, the release estimate for benzene is based on release data for methane (largest component of natural gas) from Dutch and European greenhouse gas inventories.

5.2 Exposure scenarios for humans via the environment

Gas transport covers process emissions from the high pressure transport network and release originates from service processes like flushing gas compressors and occasional start-up and breakdown emissions. Gas distribution covers the supply network delivering to the natural gas users like industrial bulk-users and power plants and households.

Besides emissions at natural gas production and transport there are releases during natural gas consumption. The major sources identified are methane slip emissions from gas engines and start-up losses at cooking, residential heating and preparation of hot-water. In the Netherlands gas engines are mainly applied

in greenhouse-farming. This sector covers about 90% of the natural gas consumption in gas engines. To some extent gas engines are also applied in the service sector and in industry, the remaining 10%. The Methane-emission factor for residential cooking and heating used in the Dutch emission inventory is 35 g/GJ natural gas burnt. For gas engines used in greenhouse farming and other sectors, two separate release factors are used, which are 409 and 250 g/GJ natural gas burnt respectively (I&M, 2011).

5.2.1 Calculation of benzene releases

The release of methane from gas production, distribution and transport and the identified consumption sources are taken from the Dutch emission inventory (ER, 2011) and amount to 12,900 ton in 2009 for natural gas transport and 3,502 ton for distribution. The total amount for transport and distribution is therefore 16,402 ton in 2009. The release from oil and natural gas extraction (flaring and venting) is about 2,690 ton, which is 14% of the total (transport, distribution and oil and gas extraction) in the Netherlands. The methane emission from natural gas consumption by households is 12,114 tons. The methane emission from green-house farming and the service sector (gas engines, cooking heating etc.) are respectively 46,473 and 5,546 tons in 2009. Methane emissions are summarized in Table 5.1.

From the European greenhouse gas inventory (EEA, 2010) the release of methane from natural gas transport and distribution for the year 1995 is reported to be 1,200 kton. Methane emissions from greenhouse farming (agriculture), the service sector and households in 1995 are respectively 9,847, 8,120 and 26,866 ton (Table 5.1). These data for the year 1995 are needed in the analysis to compare with the 1995 figures for the total benzene emissions in the EU-15 reported in the EU risk assessment report on benzene.

Table 5.1 Reported methane emissions in the Netherlands in 2009 and in the EU-15 in 1995, given in ton per year.

Source	Netherlands (2009)	EU-15 (1995)
Production (flares and vents)	2,690	130,180
Transport and distribution of natural gas	16,402	1,200,040
Households	12,114	26,866 ^a
Service sector (commercial/institutional)	5,546	8,120
Green-house farming	46,473	9,847 ^b
Total of natural gas sources	83,225	1,375,053

^a Most probably does not include emissions from start-up losses

^b It is assumed that the consumption of natural gas in agriculture is completely on account of green-house farming. The total EU-15 emission can almost completely be allocated to the Netherlands.

The data on the release of methane from natural gas transport and distribution are used to calculate the release from benzene in natural gas. For that, the composition of natural gas has to be known. In practice the majority of the customers is currently connected to the low calorific grid receiving gas that contains 0.075 % w/w benzene (see section 1.2). To evaluate the human risk that is related to the current restriction level, we assumed for our calculations that natural gas in the Netherlands contains 0.1% w/w benzene and a level of

70 % w/w methane. This results in a 700 times lower benzene emissions as compared to methane. The calculated release of benzene in the Netherlands and in the European Union (EU-15) is presented in Table 5.2.

Table 5.2 Calculated benzene releases in the Netherlands in 2009 and in the EU-15 in 1995, given in tonnes per year.

Source	Netherlands (2009)	EU-15 (1995)
Production (flares and vents)	3.8	186
Transport and distribution	23	1,714
Households	17	38
Service sector	7.9	12
Green-house farming	66	14
Total calculated release from natural gas sources	119	1,964
Total reported benzene releases	2,703	200,000
Total including release from natural gas sources	2,822	201,964
% of total benzene release attributed to natural gas sources	4.2%	1.0%

The total release of benzene in the EU-15 in 1995 is about 200,000 tonnes for the EU-15 (EC, 2008b). For 2009 the total benzene release in the Netherlands is 2,703 tonnes (ER, 2011). The releases of benzene are most likely excluding the process releases from natural gas use.

In the Netherlands the calculated contribution of benzene from natural gas to the total release of benzene is 4.2% in 2009 (Table 1). The natural gas production and distribution sector, which is outside the scope of this study, represents a share of about 1%. The green-house farming has a share of about 2.5% as releases from residential use contribute about 0.6%. The contribution on the level of EU-15 is about 1%, which can almost completely be allocated to the natural gas production and transport sector falling outside the scope of this study.

Consequences of changing the benzene limit concentration

When the benzene limit concentration for natural gas will change from 0.1 % w/w to 0.1 % v/v, the maximum benzene emissions can rise theoretically with a factor of 4.2. Under the assumption that all natural gas consumed in the Netherlands will contain 0.1% v/v benzene, the contribution of natural gas to the total benzene release would rise considerably from 4.2% (119/2822 tonnes) to 15.6% (500/3203 tonnes). This would only be the case if the benzene concentrations in gas streams would increase to the maximum permissible concentration compared to current concentration ranges.

In the European Union the air quality limit value for benzene in air is set to 5 $\mu\text{g}/\text{m}^3$ (EC, 2000; EC, 2008c). This limit value has come into force from the year 2010. In the Netherlands the annual average concentration is 0.6 $\mu\text{g}/\text{m}^3$ and does not exceed the EU-limit value. Higher local annual averages of up to 2 $\mu\text{g}/\text{m}^3$ were found for urban areas and were still 2.5 times lower than the limit value (Mooibroek et al., 2010; Velders et al. 2010 and 2011).

6 Human risk assessment

6.1 Risk characterization consumers

Four exposure scenarios were identified for consumers, which are exposure during cooking (cooking dinner and preparing tea), heating, small gas leaks and refuelling of cars. As described in Chapter 3, only exposures during cooking or due to small leaks are relevant for risk assessment of benzene for consumers. The estimated exposure to benzene in natural gas during cooking was highest during dinner cooking. Estimated concentrations with 0.1% v/v and 0.1% w/w benzene in natural gas during 60 min of cooking were $16.7 \mu\text{g}/\text{m}^3$ and $4.2 \mu\text{g}/\text{m}^3$ respectively. When considering a short peak concentration during 15 min, concentrations were $33.7 \mu\text{g}/\text{m}^3$ (0.1% v/v) and $8.0 \mu\text{g}/\text{m}^3$ (0.1% w/w).

Since acute effects will occur at levels above $80 \text{ mg}/\text{m}^3$, no acute effects are expected from exposure to the estimated peak concentrations. Therefore, 0.1% v/v benzene in natural gas does not lead to an unacceptable acute risk during cooking.

The currently estimated exposure levels are defined as concentrations in the air to which humans can be exposed by inhalation. However, for risk assessment of the carcinogenic effects, the absorbed dose of benzene is of higher importance. The estimated dose (based on 0.1% v/v) absorbed during 60 minutes of exposure to $16.7 \mu\text{g}/\text{m}^3$ corresponds to a 24 hour exposure to $0.7 \mu\text{g}/\text{m}^3$. This is lower than the dose that would be absorbed when exposed for 24 h exposure to the limit of $5 \mu\text{g}/\text{m}^3$. The estimated dose (based on 0.1% v/v) absorbed during 60 minutes of cooking plus six times boiling water for tea during 15 minutes corresponds to a 24 h exposure to $1.5 \mu\text{g}/\text{m}^3$. This is also below the dose that would be absorbed when exposed to 24 h exposure to the limit of $5 \mu\text{g}/\text{m}^3$. Therefore, there is no unacceptable risk due to benzene exposure during cooking.

The estimated exposure during a gas leak just below the odour threshold of THT for 0.1% v/v and 0.1% w/w benzene was $1186 \mu\text{g}/\text{m}^3$ and $280 \mu\text{g}/\text{m}^3$ respectively, which is far above the air quality limit of $5 \mu\text{g}/\text{m}^3$. The tracer THT is added to the natural gas to alert the user to small leaks so that proper actions are undertaken to seal them. Our estimations show that the odour THT does not protect consumers against unacceptable benzene concentrations just below the odour limit of THT.

As mentioned in section 3.2.3, it is very unlikely that the air would contain 0.03% natural gas due to gas leaks for a prolonged period of time. The natural gas concentration will either be reduced in ventilated rooms or will accumulate above the odour threshold in non-ventilated rooms. Furthermore, consumers will not stay at the same location all the time and small gas leaks are likely to develop into larger leaks that will be noticed. Although the described scenario is very unlikely, more information about the occurrence of small gas leaks is required to fully exclude an unacceptable risk.

6.2 Risk characterization workers

Seven types of activities during occupation were identified during which exposure to natural gas is plausible. It is unclear whether these activities are covered by the exception in REACH (Annex XVII, entry 5) for certain industrial processes.

For plumbing, the reasonable worst case exposure concentration was estimated to be 2.0 mg/m³ for 0.1% v/v and at 0.49 mg/m³ for 0.1% w/w. The estimated reasonable worst case exposure time for a plumber to natural gas is one hour a day. As the one hour exposure levels for both exposure scenarios are already below the occupational exposure limit of 3.25 mg/m³ (8-hour TWA), it can be concluded that the proposed change of the allowable concentration of benzene in natural gas does not result in an unacceptable risk for plumbers.

For professional cooking, no exposure estimate was made. In the risk characterization for consumers it is already concluded that there is no unacceptable risk due to gas release during cooking. Considering that the occupational exposure limit is a factor 650 higher than the air quality limit value for consumers, it is highly likely that also for cooks there is no unacceptable risk.

No exposure estimate could be made for blow off/venting, regular maintenance in gas receiving stations, sampling, manufacture and use in power stations due to the absence of relevant exposure information. Therefore, it was checked whether the maximum exposure levels that can be reached when protection is aimed against explosion were also protective for exposure to benzene. The maximal exposure to benzene when fulfilling the safety standards is 16.2 mg/m³ if the benzene concentration in natural gas is 0.1% v/v and 3.9 mg/m³ for 0.1% w/w. Both exposure levels are just (0.1% w/w) or clearly (0.1% v/v) above the occupational exposure limit of 3.25 mg/m³. Therefore, it can be concluded that the safety standard for the explosive risk is not also protecting against the risk due to exposure to benzene.

This does not mean that there is an unacceptable risk for these scenarios as the actual exposure is unknown. It is even likely that this will be lower than the maximum concentration according to the safety standard as for example the natural gas concentration will vary over time at levels below the safety standard. Workers will also work at a further distance from the source where the benzene concentration will be lower. In addition, procedures applied in blow off/venting operations and regular maintenance in gas receiving stations are such that exposure to benzene concentrations exceeding 10% of the LEL is unlikely. Workers will react to lower the exposure if 10% LEL is exceeded. Also not all workers will be exposed for 8 hours a day for their working life, which certainly accounts for employees involved in sampling. The worst case exposure time during sampling is estimated to be one hour, resulting in a possible absorbed dose for 8 hours that is below the limit of 3.25 mg/m³. It is therefore concluded that exposure during sampling does not result in an unacceptable risk for humans. Furthermore, it can be concluded that an unacceptable risk for the other industrial uses cannot be excluded but is not likely. However, exposure information on actual exposure levels (air samples), exposure duration and/or frequency is needed for most scenarios before a final conclusion can be drawn. It is remarked that it is unclear whether the described professional and industrial exposure scenarios are covered by the exception for 'substances and mixtures for use in industrial processes not allowing for the emission of benzene in quantities in excess of those laid down in existing legislation', as described in the REACH legislation.

6.3 Risk characterization environment

The contribution of releases of benzene from the identified most relevant natural gas uses to the total release of benzene in the Netherlands and in European Union (EU-15) is around 4% and 1% respectively. Considering the fact that the EU-limit value is not exceeded in the Netherlands, the contribution to the humans exposed to benzene indirectly via the environment is considered to be negligible. In the Netherlands the identified relevant sources contribute about 3% (excluding transport and distribution and venting and flares) to the total national releases of benzene.

The possible consequence of changing the benzene limit value in natural gas from 0.1% w/w to 0.1% v/v can lead to a potential increase in the release of benzene to the atmosphere with a factor of 4.2 for the identified sources and a possible rise in the total contribution to the atmospheric concentration of benzene from 4.2% to 15.2%, assuming a one on one relationship between emissions to air and atmospheric concentrations. However this would only be the case if the benzene concentrations in gas streams would increase to the maximum permissible concentration compared to current concentration ranges. Considering the current levels of benzene it is not expected that the benzene levels will rise to concentrations exceeding the EU air quality limit value.

7 Conclusions

The aim of this report was to determine if a change of the benzene restriction in natural gas from 0.1% w/w to 0.1% v/v can result in an unacceptable risk for humans. Where possible, exposure scenarios were based on data provided. Due to a lack of exposure measurements, several scenarios were based on estimations. No exposure could be estimated for some scenarios as no data was available.

The estimated exposures of consumers showed that the use of 0.1% v/v benzene in natural gas will not lead to an unacceptable risk for most plausible uses of natural gas. Although considered not likely, in case of a small gas leak consumers might be exposed to benzene concentrations that exceed the air quality limit. This exceeding of the limit applies to both 0.1 % v/v and 0.1 % w/w benzene in natural gas and is therefore not due to a change of the benzene restriction. The estimated exposures of workers showed that the use of 0.1% v/v benzene in natural gas will not lead to an unacceptable risk during plumbing or during sampling. For the other industrial uses, an unacceptable risk cannot be excluded for both 0.1% v/v and 0.1% w/w benzene levels, as the benzene concentration exceeds the occupational limit value of 3.25 mg/m³ when the concentration of natural gas reaches 0.5% (10% of the LEL). However, the likelihood of such an exposure is considered low. In addition, it is not clear whether the industrial uses are covered by the previously described exception of the REACH legislation for certain industrial processes. The estimated exposures of humans exposed via the environment showed that the use of 0.1% v/v benzene in natural gas will not lead to an unacceptable risk. Additional information is required on the scenarios for which an unacceptable risk cannot be excluded before a final conclusion for these scenarios can be drawn. For possible other uses of natural gas outside the scope of the restriction and for other gases containing benzene no risk evaluation was performed.

Calculated maximum benzene air concentrations and absorbed doses of benzene by consumer exposure or environmental exposure, using the air quality limit value of 5 µg/m³.

Exposure	Benzene concentration in air (µg/m ³)		Exposure time (h)	Exceeding safety limit?	
	0.1% w/w	0.1% v/v		0.1% w/w	0.1% v/v
<i>Consumers</i>					
Cooking dinner	4.2	16.7	1	No	No
Preparing tea	3.1	12.9	0.25	No	No
Cooking dinner + preparing tea	7.3	29.6	1.25	No	No
Small gas leak	280	1186	-	Cannot be excluded	Cannot be excluded
<i>Environmental</i>					
Annual emission	0.6	0.7	-	No	No
Max. emission	2.0	2.3	-	No	No

Calculated maximum benzene air concentrations and absorbed doses of benzene by occupational exposure, using the occupational exposure limit of 3.25 mg/m³.

Exposure	Benzene concentration in air (mg/m ³)		Exposure time (h)	Exceeding safety limit?	
	0.1% w/w	0.1% v/v		0.1% w/w	0.1% v/v
<i>Workers</i>					
Plumbers	0.49	2.0	1	No	No
Blow off/venting ^a	3.9	16.2	8	Cannot be excluded	Cannot be excluded
Maintenance gas receiving station ^a	3.9	16.2	8	Cannot be excluded	Cannot be excluded
Sampling ^a	3.9	16.2	<1	No	No
Manufacture of other substances ^a	3.9	16.2	8	Cannot be excluded	Cannot be excluded
Use in power stations ^a	3.9	16.2	8	Cannot be excluded	Cannot be excluded

^a Calculations based on the maximum exposure level protective against explosion, which is 0.5% natural gas in air.

8 References

Aardgasauto.com (2013). <http://www.aardgasauto.com/video's.html?cat=44>

Brett SM, Rodricks JV and Chinchilli VM (1989). Review and update of leukaemia risk potentially associated with occupational exposure to benzene. *Env Health Perspect* 82: 267-281.

ConsExpo 4.1 (2007).

<http://www.rivm.nl/en/healthanddisease/productsafety/ConsExpo.jsp>

Crump KS and Allen B (1984). Quantitative estimates of risk of leukaemia from occupational exposure to benzene. *Occupational Safety and Health Administration, Docket H-059B*.

Crump KS (1994). Risk of benzene-induced leukaemia: a sensitivity analysis of the Pliofilm cohort with additional follow-up and new exposure estimates. *J Toxicol Environ Health* 42: 219-42.

EC (1992). Occupational exposure limits. Recommendations of the Scientific Expert Group 1991-1992. EUR 15091. The Scientific Committee on Occupational Exposure Limits (SCOEL).

EC (1998). Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC. 1998L0070.

EC (1999a). Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations. *Official Journal of the European Communities*. L 200.

EC (1999b). Council directive on ambient air quality assessment and management. Working group on benzene. Commission of European Communities.

EC (2000). Directive 2000/69/EC of the European Parliament and the Council. of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air. *Official Journal of the European Communities*. L313.

EC (2006a). Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency. Annex XVII, entry 5. *Official Journal of the European Union*.

EC (2006b). Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency. Article 2.1.d. *Official Journal of the European Union*.

EC (2008a). Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

EC (2008b). European Union Risk Assessment Report, Benzene. European Commission.

EC (2008c). Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union. L 152.

ECHA (website). "Registered substances. Chemical Substance Search." European Chemicals Agency (ECHA) From: <http://echa.europa.eu/web/guest/information-onchemicals/registered-substanceslist>, last update 27 March 2013.

EEA (2010). Annual European Union greenhouse gas inventory 1990-2008 and inventory report 2010. Technical report No 6.2010, URL: <http://www.eea.europa.eu/publications/european-union-greenhouse-gas-inventory-2010>

ER (2011). Dutch Pollutant Release and Transfer Register (Emissieregistratie). Data retrieved through the confidential website is based on the dataset 'ER Reeks 1990-2009 Definitief'. For the public website see URL: <http://www.emissieregistratie.nl/>

EPA (2013). Substance Registry Services of the Environmental Protection Agency http://iaspub.epa.gov/sor_internet/registry/substreg/searchandretrieve/advance_dsearch/externalSearch.do?p_type=SRSITN&p_value=157586

Gasunie (2009) Instructie afblazen from the Operations management handbook Code OMH_4.4.3-15.

GTS (1988). Physical properties of natural gas. Gas Transport Services (GTS). <http://www.gastransportservices.nl/uploads/fckconnector/f3f60835-79d1-4f95-8466-3af3d4c70238>.

I&M (2011). Stationary combustion fossil fuels, version 1.0, status definitive, March 2011. Protocol 11-002. Ministry of Infrastructure and Environment (I&M).

ISO 10715 (1997). International organisation for Standardisation, Switzerland reference number ISO 10715:1997(E).

IVM (undated). Veiligheid voor Operationeel Leingevenden VCA, Instituut voor Veiligheid en Milieu b.v.

De Jong FMW, Janssen MPM (2011). Luchtnormen voor 31 prioritaire stoffen. National Institute for Public Health and the Environment (RIVM). Report 601357003/2011.

Mooibroek D, Beijk R and Hoogerbrugge R (2010). Air quality in the Netherlands in 2009. National Institute for Public Health and the Environment (RIVM). Report 680704011.

NEN-EN 437 (2009). Test gases, test pressures and categories of appliances. European standard prepared by the Technical Committee CEN/TC 238, document EN 437:2003+A1:2009.

NEN 7244-1 (2003). Dutch edition on base of NEN-EN 12007-1 – Gas supply systems – Pipelines for maximum operating pressure up to and including 16 bar – Part 1: General functional recommendations. Document NEN 7244-1:2003.

NGV-Holland (2012). Overview of natural gas refuelling stations in the Netherlands. Last update: June 11 2012. <http://www.ngv-holland.nl>.

NMA (2011). Connection and transport conditions, according to Article 12b of the Dutch Gas Law. Netherlands Competition Authority. <http://www.nma.nl/images/Aansluit-%20en%20transportvoorwaarden%20Gas%20%20RNB22-154495.pdf>

Otte PF, Lijzen JPA, Mennen MG and Spijker J (2007). Guidance on air quality measurements for assessing risks of contaminated soil. National Institute for Public Health and the Environment (RIVM). Report 711701048.

Rinsky RA, Young RJ, Smith AB (1981). Leukemia in benzene workers. *Am J Ind Med.*, 2(3): 217-45.

Rinsky RA, Smith AB, Hornung R, Filloon TG, Young RJ, Okun AH, Landrigan PJ. (1987). Benzene and leukemia. An epidemiologic risk assessment. *N Engl J Med.*, 316(17): 1044-50.

SER (2013). Website of the Social and Economic Council of the Netherlands. www.ser.nl.

Velders GJM, Aben JMM, Diederens HSMA, Drissen E, Geilenkirchen GP, Jimmink BA, Koekoek AF, Koelemeijer RBA, Matthijsen J, Peek CJ, van Rijn FJA, de Vries WJ (2010). Concentratie kaarten voor grootschalige luchtverontreiniging in Nederland. Report 2010. Netherlands Environmental Assessment Agency (PBL), Bilthoven.

Velders GJM, Aben JMM, Jimmink BA, van der Swaluw E, de Vries WJ (2011). New maps of concentrations and depositions for NSL and PAS. National Institute for Public Health and the Environment (RIVM). Report 680362001.

WHO (2000). Air quality guidelines for Europe; second edition. Copenhagen, Denmark, World Health Organization. Report No. 91.

Wong O and Raabe GK (1995). Cell-type-specific leukemia analyses in a combined cohort of more than 208,000 petroleum workers in the United States and the United Kingdom, 1937-1989. *Regul Toxicol Pharmacol.* 21:307-21.

9 Appendix 1 Actual benzene content natural gas

The G-gas delivered to households is composed of 1) Groningen gas, 2) imported gas and 3) gas from small fields. A conservative estimate of the average benzene concentration can be established as follows:

- The benzene concentration in gas from small fields is sometimes higher than 0.1 % w/w but always less than 0.1 % v/v. For the calculation of the benzene content in the grid, the total volume of gas from small fields is assumed to contain 0.1 % v/v benzene (= 0.42 % w/w).
- The benzene concentration in imported gas streams varies from source to source, but is always less than 0.1 % w/w. For the calculation of the benzene content in the grid, the total volume of imported gas is assumed to contain 0.1 % w/w benzene.
- The benzene content in Groningen gas is known: 0.075 % w/w.

The total gas volumes and related benzene concentrations can thus be summarized as follows:

Source	Volume (bln Nm³)	Benzene concentration (w/w)
Groningen	50.86 ^a	0.075 %
Import	29.56 ^b	0.1 %
Small fields	30.58 ^a	0.42 %

^ahttp://www.nlog.nl/resources/Jaarverslag2010/Aardgas_productie_2010_+_Historische_productie.pdf

^b Calculated from total natural gas volume of 111 bln Nm³ (annual report GTS 2010) minus the volume of Groningen gas and minus gas from small fields.

10 Appendix 2 Calculations consumer exposure

Exposure due to cooking

A consumer (60 kg) cooks daily on a natural gas cooker/stove, without electronic ignition. It's assumed that the stove ring has two cooking rings with an ignition capacity of 0.15 kWh and two rings with an ignition capacity of 0.5 kWh. The four rings are assumed to be used simultaneously for preparing dinner. One of the rings with an ignition capacity of 0.5 kWh is assumed to be used additionally 6 times per day boiling water for tea. It's assumed that it takes 5 seconds each time to ignite the flame. When preparing the dinner the delay time igniting the gas between the individual rings of 30 seconds is used. Therefore it will take four matches to prepare a dinner. The room volume of the kitchen is 15 m³ and the kitchen is ventilated 2.5 times/h (Concept 4.1). Assuming the person forgets to turn on the cooking hood during the cooking, there will be no additional ventilation of the kitchen. Assuming the natural gas contains 0.1% v/v or 0.1% w/w benzene, the consumer will inhale benzene. The benzene will be instantaneously dispersed throughout the kitchen along with the natural gas. It's assumed that the cooking of the dinner takes 60 minutes. The boiling of water and preparing tea will take 15 minutes. It is assumed that the consumer stays in the kitchen during cooking dinner and preparing tea. The temperature in the kitchen is set to 20 °C.

Calculation cooking exposure

Per second a ring with a capacity of 0.15 kWh generates 4.72×10^{-6} (m³) gas and a ring with a capacity of 0.5 kWh generates 1.57×10^{-5} (m³) gas per second.

In 5 seconds the four rings of the stove generate:
 $5 \text{ (s)} \times 2 \times (4.72 \times 10^{-6} \text{ (m}^3\text{)} + 1.57 \times 10^{-5} \text{ (m}^3\text{)})$
 $= 2.04 \times 10^{-4} \text{ (m}^3\text{) natural gas}$

The overpressure of the service pipe is 30 mbar and the pressure in the kitchen is 101000 Pa (1 atm), therefore the pressure in the pipe is (3000 + 101000 Pa = 104000 Pa). When the gas is released from the service pipe it is decompressed. Therefore the volume will increase.

According to the algorithm ($p_1 \times v_1 = p_2 \times v_2$) the volume of the natural gas in the kitchen will be:

p_1 = pressure service pipe (Pa = N/m²)
 v_1 = volume gas in service pipe (m³)
 p_2 = pressure kitchen (Pa = N/m²)
 v_2 = volume gas in kitchen (m³)

$(2.04 \times 10^{-4} \text{ (m}^3\text{)} \times 104000 \text{ (Pa)}) / 101000 \text{ (Pa)} = 2.1 \times 10^{-4} \text{ (m}^3\text{) at } 20 \text{ }^\circ\text{C (293 Kelvin)}$

The algorithm of the ideal gas law is: $P \times V = n \times R \times T$
 Therefore, at 293 Kelvin, $n = (P \times V)/(R \times T)$ at 293 Kelvin,
 $2.1 \times 10^{-4} \text{ (m}^3\text{)}$ natural gas with 0.1% v/v benzene contains:

Where:

n = amount of substance of gas (mol)
 P = pressure kitchen ($\text{Pa} = \text{N/m}^2$)
 V = volume gas in kitchen (m^3)
 R = universal, gas constant = 8.314 (N.m/Kmol)
 T = temperature kitchen ($\text{K} = \text{Kelvin}$)

$n = ((101000 \text{ (N/m}^2\text{)} \times 0.1\% \text{ (v/v)} \times 2.1 \times 10^{-4} \text{ (m}^3\text{)}) / (8.31 \text{ (N.m/Kmol)} \times 293 \text{ (K)})) = 8.7 \times 10^{-6} \text{ mol}$
 $= 8.7 \times 10^{-6} \text{ (mol)} \times 78.1 \text{ (mol weight benzene)} = 0.68 \text{ (mg) benzene}$

With the ConsExpo inhalation model for instantaneous release the mean air concentration of benzene in the air was calculated for the first 15 minutes and one hour.

ConsExpo calculated for natural gas containing 0.1% v/v benzene:
 a mean $t=15 \text{ min}$ of $33.7 \text{ }\mu\text{g/m}^3$
 a mean $t=60 \text{ min}$ of $16.7 \text{ }\mu\text{g/m}^3$.

By using a reduction factor of 4.2 (see below) for natural gas containing 0.1% w/w benzene the benzene concentration calculated is:
 a mean $t=15 \text{ min}$ of $8.0 \text{ }\mu\text{g/m}^3$
 a mean $t=60 \text{ min}$ of $4.0 \text{ }\mu\text{g/m}^3$

For detailed information see Appendix 3: outputs ConsExpo.

Calculation tea exposure

The consumer boils tea water and is exposed during 15 minutes (in total 6 events). Replacing the amount of natural gas released during cooking dinner by the amount of natural gas released during boiling water the amount benzene released in the kitchen was calculated.

The amount of natural gas released due to boiling water in 5 seconds is:
 $5 \text{ (sec)} \times 1.57 \times 10^{-5} \text{ (m}^3\text{)} = 7.85 \times 10^{-5} \text{ (m}^3\text{)}$.

Using the same formula as for preparing dinner: 0.26 mg benzene is released.

With the ConsExpo inhalation model for instantaneous release the mean air concentration of benzene in the air was calculated for the first 15 minutes.

ConsExpo calculated for natural gas containing 0.1% v/v benzene:
 a mean $t=15 \text{ min}$ of $12.9 \text{ }\mu\text{g/m}^3$

By using a reduction factor of 4.2 (see below) for natural gas containing 0.1% w/w benzene the benzene concentration calculated is:
 a mean $t=15 \text{ min}$ of $3.1 \text{ }\mu\text{g/m}^3$

For detailed information see Appendix 3: outputs ConsExpo.

Note: according to the ideal gas law at 293 Kelvin, one cubic meter gas contains: $= ((101000 \text{ (Pa)} \times 1) / (8.31 \times 293 \text{ (k)})) = 41.48 \text{ mol gas}$.
 Therefore natural gas 0.1% v/v benzene contains:

$0.1\% \times 41.48 \text{ (mol)} \times 78.1 \text{ (g/mol)} = 3.24 \text{ gram benzene per m}^3$.

The molecular weight of natural gas depends on the composition of the gas. The molecular weight of "Groninger gas" is 18.65 (g/mol). Assuming the natural gas has a molecular weight of 18.65 (g/mol), one cubic meter natural gas weighs: $41.48 \text{ (mol)} \times 18.65 \text{ (g/mol)} = 773.6 \text{ g}$. Therefore the weight of 0.1% w/w benzene is 0.77 g.

Natural gas with 0.1% w/w benzene contains a factor 4.2 less benzene than natural gas with 0.1% v/v benzene.

Exposure due to small gas leaks

Gas leak exposure

Theoretically a consumer with a normal developed sense of smell can be exposed to air containing 0.03 % natural gas, without smelling the odour of THT (Otte et al., 2007).

Gas containing 0.1% v/v benzene

According to the ideal gas law at 293 Kelvin, one cubic meter benzene contains 41.48 mol gas

$0.1\% \text{ (v/v)} \times 0.03\% \times 41.48 \text{ (mol)} \times 78.1 \text{ (g/mol)}$
 $= 1186 \text{ } \mu\text{g benzene per m}^3$.

Gas containing 0.1% w/w benzene

By using a reduction factor of 4.2 for natural gas containing 0.1% w/w benzene, the benzene concentration is:

$1186 \text{ (}\mu\text{g/m}^3) / 4.2 = 280 \text{ } \mu\text{g benzene per m}^3$.

11 Appendix 3 Outputs ConsExpo

ConsExpo 4.1 Cooking dinner the first 15 minutes report**Product**

natural gas

Compound

Compound name :	benzene	
CAS number :	71-43-2	
molecular weight	78.1	g/mol
vapour pressure	1E4	Pascal
KOW	2.13	10Log

General Exposure Data

exposure frequency	365	1/year
body weight	60	kilogram

Inhalation model: Exposure to vapour : instantaneous release

weight fraction compound	1	fraction
exposure duration	15	minute
room volume	15	m3
ventilation rate	2.5	1/hr
applied amount	0.68	milligram

Uptake model: Fraction

uptake fraction	1	fraction
inhalation rate	32.9	m3/day

Output**Inhalation (point estimates)**

inhalation mean event concentration :	0.0337	mg/m3
inhalation mean concentration on day of exposure:	0.000351	mg/m3
inhalation air concentration year average :	0.000351	mg/m3/day
inhalation acute (internal) dose :	0.000193	mg/kg
inhalation chronic (internal) dose :	0.000192	mg/kg/day

Integrated (point estimates)

total external dose:	0.000193	mg/kg
total acute dose (internal):	0.000193	mg/kg
total chronic dose (internal):	0.000192	mg/kg/day

ConsExpo 4.1 Cooking dinner the 60 minutes report

Product

natural gas

Compound

Compound name :	benzene	
CAS number :	71-43-2	
molecular weight	78.1	g/mol
vapour pressure	1E4	Pascal
KOW	2.13	10Log

General Exposure Data

exposure frequency	365	1/year
body weight	60	kilogram

Inhalation model: Exposure to vapour : instantaneous release

weight fraction compound	1	fraction
exposure duration	60	minute
room volume	15	m3
ventilation rate	2.5	1/hr
applied amount	0.68	milligram

Uptake model: Fraction

uptake fraction	1	fraction
inhalation rate	32.9	m3/day

Output

Inhalation (point estimates)

inhalation mean event concentration :	0.0166	mg/m3
inhalation mean concentration on day of exposure:	0.000694	mg/m3
inhalation air concentration year average :	0.000693	mg/m3/day
inhalation acute (internal) dose :	0.00038	mg/kg
inhalation chronic (internal) dose :	0.00038	mg/kg/day

Integrated (point estimates)

total external dose:	0.00038	mg/kg
total acute dose (internal):	0.00038	mg/kg
total chronic dose (internal):	0.00038	mg/kg/day

ConsExpo 4.1 preparing tea report**Product**

natural gas

Compound

Compound name :	benzene	
CAS number :	71-43-2	
molecular weight	78.1	g/mol
vapour pressure	1E4	Pascal
KOW	2.13	10Log

General Exposure Data

exposure frequency	365	1/year
body weight	60	kilogram

Inhalation model: Exposure to vapour : instantaneous release

weight fraction compound	1	fraction
exposure duration	15	minute
room volume	15	m3
ventilation rate	2.5	1/hr
applied amount	0.26	milligram

Uptake model: Fraction

uptake fraction	1	fraction
inhalation rate	32.9	m3/day

Output**Inhalation (point estimates)**

inhalation mean event concentration :	0.0129	mg/m3
inhalation mean concentration on day of exposure:	0.000134	mg/m3
inhalation air concentration year average :	0.000134	mg/m3/day
inhalation acute (internal) dose :	7.36E-5	mg/kg
inhalation chronic (internal) dose :	7.36E-5	mg/kg/day

Integrated (point estimates)

total external dose:	7.36E-5	mg/kg
total acute dose (internal):	7.36E-5	mg/kg
total chronic dose (internal):	7.36E-5	mg/kg/day

12 Appendix 4 Calculations occupational exposure

Exposure scenario 1: Maintenance work in a residence basement.

Calculation at a benzene concentration in natural gas of 0.1% v/v

5 L gas may be released into the surroundings when assuming a gas pipeline of 10 meters with a diameter of 2.5 cm and an overpressure of gas of 30 mbar (104000 Pa; $p \cdot V = \text{constant}$). This is the sum of the volume of gas from the gas meter to the workplace as well as the end of the pipeline into the workplace. The volume of benzene in 5 L gas (0.1% v/v) is 0.005 L benzene. The number of moles of benzene (n) can be calculated with the ideal gas law ($PV = nRT$), assuming T is 293 K = 20°C. Multiplication of n with the molecular weight of benzene (78.1) makes 16.37 mg benzene.

The benzene concentration in the near field (8 m³) of the worker will be $16.37/8 = 2.05 \text{ mg/m}^3$. A reasonable worst case estimate of the average work duration in the basement is 1 hour.

Calculation at a benzene concentration in natural gas of 0.1% w/w

5 L gas will be released into the surroundings (see above). This is 0.21 moles ($=5/24$, assuming a molar gas volume of 24 L at 20 °C). The mass of 0.21 moles gas is 3.93 g (molar mass natural gas = 18.65 g). The benzene mass (0.1% w/w) in 3.93 g natural gas is 3.93 mg.

The benzene concentration in the near field (8 m³) of the worker will be $3.93/8 = 0.49 \text{ mg/m}^3$. A reasonable worst case estimate of the average work duration in the basement is 1 hour.

