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Benzene in Gasoline and Crude Oil: Occupational and Environmental Implications

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A review of studies, published in peer-reviewed journals and articles available as technical reports of various organizations, regarding benzene in gasoline and crude oil was performed. The summarized data will be useful for retrospective exposure assessments in epidemiological studies. It shows that in the past, benzene in gasoline has been quite high, but now, there is a distinct trend in North America and Europe to reduce benzene in gasoline to a level of about 1%. The reduction of benzene in gasoline results not only in the lowering of occupational exposure for workers, but it also has far greater influence in decreasing the environmental benzene exposure for the general public.

Keywords: benzene, gasoline, crude oil, percentage benzene

Benzene has been recognized as a toxic chemical capable of causing both acute and chronic poisoning.[1,2] Chronic effects center on the blood forming system and lead to the possible induction of leukemia—a major concern.[3] Benzene is a natural constituent of crude oil and is also found in varying concentrations in refined products such as gasoline.[4] Benzene is present in gasoline as a result of its natural occurrence in crude oil. It is also a byproduct formed during the processing of crude oil. In the past, as lead antiknock additives were reduced and eliminated, more aromatics (including benzene) were blended into gasolines to compensate for antiknock purposes. Processes have now changed. The focus is to reduce the benzene content.

The magnitude of exposure is greatest for those individuals occupationally exposed to benzene; however, a far greater number of individuals are exposed as a result of benzene released from gasoline filling stations, from auto exhaust emissions, and from the use of tobacco products. In assessing the occupational exposure to benzene of workers in the petroleum industry, as well as in other sectors that use petroleum products such as gasoline, one needs to know the percentage content of benzene. All else being equal, a higher benzene content would result in a higher benzene exposure compared with a low benzene content product. The data on benzene content of crude oil and gasoline is scattered in the literature and not readily available to the industrial hygiene community. For example, it has been reported that benzene is found in gasoline from trace amounts to as much as 30% in some countries,[1] but the details are not readily available. Benzene's threshold limit value-time weighted average (TLV-TWA) has been greatly reduced to 0.5 ppm,[1] so information regarding benzene content in a summary format would be useful to industrial hygiene practitioners.

The objective of this short communication is to provide summarized information regarding benzene in crude oil and gasoline and briefly discuss its occupational and environmental implications.

METHODOLOGY

An extensive literature review was conducted. Bibliographic databases including NIOSH-TIC, CISILO, and Science Citation Index were searched using keywords such as *percent benzene*. All issues of key industrial hygiene publications such as the *American Industrial Hygiene Association Journal*, the *Annals of Occupational Hygiene*, the *Applied Occupational and the Environmental Hygiene* were searched manually. Available technical reports of various organizations such as the American Petroleum Institute, the Canadian Petroleum Product Institute, and the oil companies' European organization for environment and health protection (CONCAWE)

TABLE I. Benzene in Crude Oil and Gasoline Samples

Author	Benzene (%) N	AM	Min	Max	Comments on Method of Analysis[A]
CRUDE OIL					
Grizzle & Coleman (1979)[5] US 15 geological age samples (mainly taken from around US and few from Kuwait & North Sea)					wt % analyzed by GC/FID using backflushing technique, detection
Total crude oil samples	102	0.16	nd	0.71	limit self-imposed 10 ppm
Drummond (1991)[60] Canada (from 8 different areas within Canada)					wt % analyzed by GC/MS
Crude oil	37	0.33	0.08	0.94	
GASOLINE					
European–Gasoline Samples					
Parkinson (1971)[7]					volume % reported
Data from 1969					no details given on how determined
Gasoline measured from retail station	9		2.8	5.8	
Gasoline measured from rail site	5		0.4	0.7	
Gasoline measured from rail site	3		1.3	3.1	
Gasoline measured from road site	4		6.8	6.8	
Motor gasoline containing added benzene	3		10	33	
Sherwood (1972)[8]					wt % reported
Normal petrol		~2.7			no details given on how determined
Premium petrol		~4.5			
CONCAWE (1987)[9]					wt % reported
Data from 1984–85					no details given on how determined
Aromatics (carbon no. 6) European gasolines		4.0	1.5	6.5	
CONCAWE Report 89/57 (1989)[10]					volume % reported
(Data from 16 countries: Austria, Belgium, Denmark, Finland, France, Greece, Italy, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, U.K., West Germany, Yugoslavia)					measured but does not state how done as article concerned with economics—information was collected for each European country
Regular low leaded gasoline	162	1.7	0.3	7.6	All values are weighted means
Premium low leaded gasoline	243	2.8	0.5	8.0	
Premium leaded gasoline	236	2.3	0.5	8.6	
Regular unleaded gasoline	124	2.4	0.3	4.7	
Premium unleaded gasoline	181	3.3	0.3	5.7	
+All leaded	641	2.34	0.3	8.6	
+All unleaded	305	2.93	0.3	5.7	
Gallagnani, Garrigues, & Guardia (1994)[11]					volume % reported
Premium unleaded petrol	2	2.47	1.74	3.20	FA FTIR method developed
Leaded petrol	3	2.71	1.80	3.26	Detection limit for benzene is 0.002% v/v.
Hakkola & Saarinen (1999)[12] Finland					volume % reported
Data from 1996			3.1	3.8	no details given on how determined
CONCAWE Report 5/98 (1998)[13]					volume % reported
(Data from 1996 survey from 16 different countries–Austria, Belgium, Denmark, Finland, France, Germany, U.K., Greece, Hungary, Italy, Netherlands, Norway, Portugal, Spain, Sweden & Switzerland)					GC analysis + All values are weighted means
+All leaded gasoline (reg L 92, Sup L 86,97,98)	170	1.72	0.3	3.9	
+All unleaded gasoline (reg UL 91,92 & Sup UL 95,98)	889	1.88	0.3	4.9	
Vainotalo et al. (1999)[14] Finland					weight % reported
Data from 1996		0.7–<1			Samples were collected in glass bottles, which were tightly sealed and transferred to a test lab of the gasoline supplier for GC analysis Authors determined that their value of 0.75% w/w corresponded to 0.64% v/v.
USA—Gasoline Samples					
U.S. Army report (1972)[15]					volume % reported
(Referenced in Runion 1975)					
Unleaded and low-lead gasoline	37	0.8		2.0	
Runion (1975)[16]					volume % reported
Data reviewed from 1970–75		<1		1.3	
NIOSH (1976)[17]					volume % reported
Referenced in Cheremisinoff (1979)	18		1.0	1.7	no details given

TABLE I. Continued.

Author	Benzene (%) N	AM	Min	Max	Comments on Method of Analysis[A]
EPA (1978)[18]					volume % reported
Referenced in EPA (1984)		1.3	0.15	4.26	gas chromatography
Runion (1977)[19]					typical liquid volume % of benzene in
Data from 1977					Gulf U.S. Gasoline Oct. 1976
Grades of gasoline—					no details on how determined
Good Gulf	6	1.24	0.54	1.99	
Gulf Crest,	6	1.25	0.82	1.98	
No Nox	6	1.26	0.81	2.39	
McDermott & Vos (1979)[20]					volume % reported
Data from 1977					Method used was chromatographic
Regular			0.47	1.17	analysis.
Unleaded			0.42	1.74	
Premium			0.41	1.69	
Tironi et al. (1986)[21]					mass % reported
Data from 1985					GC analysis
Winter gasoline	1	3.16			
Summer gasoline	1	3.18			
Poole et al. (1988)[22]					volume % reported
Regular unleaded gasoline	20	1.22			GC/FID method developed using a
Premium grade unleaded gasoline	20	1.29			single column.
Clayton (1991)[23]					volume % reported
Data from 1990 (Cincinnati, Phoenix, & Los Angeles)					
Regular leaded	3	1.8	1.3	2.7	
Regular unleaded	6	1.7	0.9	2.6	
Midgrade unleaded	3	1.3	0.6	2.6	
Super unleaded	6	1.5	0.35	4.1	
MVMA (1990)[24] (referenced in Tironi & Hodgkins (1991)					volume % reported for U.S. unleaded
1987–1990 data (for winter and summer, regular unleaded and premium unleaded)					gasolines MVMA national survey, 1987–1990
					approx. 400 data points from commercial service station from around the U.S.
	total ~400	1.35–1.73	<0.10	5.18	no details on how determined
Hartle (1993)[25]					volume % reported
Data from 1990 (Cincinnati, Phoenix, & Los Angeles)					Samples analyzed using GC/FID
(regular, premium, super)	75	0.39–2.00		3.1	according to NIOSH method 1615.
Backer et al. (1997)[26] Alaska					wt % reported
Data from 1995					determined by EPA GC analyses
Regular gasoline		5.2			probably same size is one for each type
E-10 blend gasoline		4.4			
Canadian–Gasoline Samples					
PACE Report 87-5 (1987)[27]					wt % reported
Data from 1985 summer study					chromatography GC/FID bulks diluted
Regular leaded	19	1.9	0.08	3.3	in CS2
Regular unleaded	19	2.2	0.1	5.2	
Super unleaded	19	1.2	0.1	4.9	
PACE Report 89-3 (1989)[28]					wt % reported
Data from 1986 winter study					chromatography GC/FID bulks diluted
Regular leaded	20	1.5	0.3	4.1	in CS2
Regular unleaded	20	2.2	0.4	4.7	
Super unleaded	18	2.2	0.4	5.7	
Alberta Research Council (1991)[29]					volume % reported
Data from 1989–90 (5 regions)					gas chromatography method data
Regular leaded	117	1.56	0.27	4.30	calculated as mass % and volume %
Regular unleaded	134	1.75	0.34	3.90	
Premium unleaded	118	2.39	0.14	5.52	
Environment Canada 5/HA/6 (1996)[30]					volume % reported
Data from 1994 (Atlantic/Quebec, Ontario & West) (regular unleaded, midgrade unleaded & premium unleaded)					methods used are capillary GC specified
All Canada	2126	1.6	0.0	5.5	Total of 18 refineries and 4 importers participated in the survey.

TABLE I. Continued.

Author	Benzene (%) N	AM	Min	Max	Comments on Method of Analysis[A]
Environment Canada (1999)[31]					% volume reported
Data from 1998 (Atlantic/Quebec, Ontario & West)					methods used are capillary GC
Regular unleaded	1833	1.5	0.1	6.9	specified
Mid-grade unleaded	18	2.0	1.4	3.1	Total of 19 refineries/importers
Premium unleaded	587	2.0	0.1	5.7	participated in the survey; however,
All Canada (total)	2440	1.6	0.1	6.9	4 did not report results. Thus, info
Data from 1994–1998[31]					based on 15.
All Canada		1.4–1.6			
Other Countries—Gasoline Samples					
Ikeda (1984)[32] Japan					volume % reported
Data from 1983 (14 cities across country studied)					capillary GC/FID determination
Automobile gasoline	214	1.39	0.91	2.08	
Foo (1991)[33] Singapore					% reported (but does not state by vol
Regular	5	2.7	1.8	3.4	or by weight)
Premium	5	2.8	2.0	3.7	no details on how bulk samples analyzed

[A]GC = gas chromatography; FID = flame ionization detector; MS = mass spectroscopy; FA FTIR = flow analysis Fourier transform infrared.

were also reviewed. Accessible government documents from Environment Canada and the U.S. Environmental Protection Agency (EPA) also were included.

RESULTS

The data from the accumulated literature has been summarized in Table I. The number of samples (N), arithmetic mean (M), minimum (MIN), and maximum (MAX) values, and the salient details regarding method of analysis (Comment on Method of Analysis) have been reported where available.[5–33]

DISCUSSION

The data listed in the table shows that the benzene in crude oil is relatively low, at less than 1.0% by weight, with mean values of 0.16% by weight and 0.33% by weight reported. The percentage benzene in gasoline, on the other hand, has been much higher. In Europe as high as 8.6% by volume benzene was reported in a 1989 study.[10] Mean values of 1 to 4% have been prevalent. From data collected in 1969, Parkinson[7] reported a benzene value as high as 33% by volume. He stated that all motor gasolines contain benzene, and that it is unusual for the amount to exceed 5% by volume except when special refining techniques have been used or benzene has been added to the gasoline, as in this situation. In North America the benzene content in gasoline is generally lower than in Europe. The maximum value reported in the United States is 5.18% by volume,[24] and most mean values are around 2%. Canadian gasoline has been reported to contain as high as 6.9% by volume,[31] but the mean values are at a similar level at around 2.0%. Only limited data were found from other countries, where the maximum reported was 3.7% and the mean value 2%.

Gasoline is a complex mixture of volatile hydrocarbons, containing as many as 250 hydrocarbons, with substantial variation depending on the source of crude oil, refinery processes, and so forth. A typical modern gasoline composition would be 80% paraffins, 14% aromatics, and 6% olefins.[4] The reporting of benzene in gasoline is either by weight percentage or volume percentage. It has been shown that measurement of 0.75% (w/w) is equivalent to 0.64% (v/v).[14] In general, benzene in gasoline given as weight percentage is slightly higher than volumes percentage, and this should be kept in mind when interpreting the data in Table I. Percentage volume or percentage weight have been indicated, in the text and in the table, where information is available. When it is not available, data have been reported simply as "%." The difference between percentage by volume and percentage by weight is around 15% (where 0.64% volume = 0.75% weight). At the levels that benzene is found in gasoline (1–5%) , this amount is not that significant because we are dealing with low numbers.

Although the magnitude of exposure to benzene is greatest for individuals occupationally exposed to benzene (those employed in the petroleum industry), a far greater number of individuals are exposed as a result of benzene being released in the environment from exhaust and evaporative emissions. Benzene also is emitted from diesel engines, but at levels approximately one-fortieth of that coming from gasoline vehicles.[34,35] According to EPA,[34,35] on a mass basis, benzene makes up about 70% of the total amount of the gaseous toxics. Thus, if toxic emissions are to be controlled through mobile sources, the benzene content of gasoline is an obvious area for priority consideration. Refiners can directly control benzene levels, and benzene offers refiners the greatest degree of control over a specific toxic fuel component that is also present in emissions at substantial levels. Reducing the benzene content in gasoline because of environmental concerns will result, in turn, in reducing the occupational exposure due to benzene in gasoline for those employed in the petroleum industries.

The current U.S. Reformulated Gasoline (RFG) program, which affects about one-third of all gasoline sold in the United States, includes regulations for benzene content and toxic emissions. This program requires that no batch of RFG may have a benzene content exceeding 1.0% by volume.[34,35] The conventional gasoline standards are often referred to as the antidumping requirements because they prevent refiners from merely directing the clean gasoline to RFG areas and dumping the dirtier fuel in all other areas. EPA does not currently regulate the benzene level of conventional gasoline, but it appears that it is being kept at

around 1% by volume. In Europe the legal specification for benzene in gasoline was up to 5%, but as of January 1, 2000, the legal specification is now a maximum of 1% by volume. This was already preceded in some countries (Italy, Finland) by a few years.[36] In Canada, regulations published on November 26, 1997, prohibit the supply after July 1, 1999, of gasoline that contains benzene at a concentration exceeding 1.0% by volume. They also prohibit the sale or the offer for sale of gasoline that contains benzene at a concentration that exceeds 1.5% by volume after July 1, 2000, in the northern supply area and October 1, 1999, for everywhere else in Canada.[37]

CONCLUSIONS

Benzene content in gasoline in the past has been high. The summarized data would be useful for retrospective exposure assessments in epidemiological studies. There currently is a distinct trend in North America and Europe to reduce benzene in gasoline to about 1% by volume. Such reductions will not only benefit workers occupationally exposed to benzene, but also will have a concomitant effect of significantly reducing environmental benzene exposure for the general public.

REFERENCES

1. **American Conference of Governmental Industrial Hygienists (ACGIH):** Documentation of TLV for benzene. In *Chemical Substance TLVs and BEIs—2000.* Cincinnati, Ohio: ACGIH, 2000.
2. **Agency for Toxic Substances and Disease Registry (ATSDR):** *Draft Toxicological Profile for Benzene*. Atlanta: ATSDR, 1995.
3. **Finkelstein, M.M.:** Leukemia after exposure to benzene. *Am. J. Ind. Med. 38*:1–7 (2000).
4. **American Conference of Governmental Industrial Hygienists (ACGIH):** Documentation of TLV for gasoline. In *Chemical Substance TLVs and BEIs—2000.* Cincinnati, Ohio: ACGIH, 2000.
5. **Grizzle, P.L., and H.J. Coleman:** Gas chromatographic determination of benzene and toluene in crude oils. *Anal.Chem. 51*:602–608 (1979).
6. **Drummond, I.:** Industrial Hygiene Survey Report: Benzene Content of Crude Oil and Condensate Streams. Calgary, Alberta: Esso Resources Canada Ltd., 1991.
7. **Parkinson, G.:** Benzene in motor gasoline—an investigation into possible health hazards in and around filling stations and in normal transport operations. *Ann. Occup. Hyg. 14*:145–153 (1971).
8. **Sherwood, R.J.:** Evaluation of exposure to benzene vapour during the loading of petrol. *Brit. J. Ind. Med. 29*:65–69 (1972).
9. **CONCAWE:** *A Survey of Exposures to Gasoline Vapour* (CONCAWE Report no. 4/87). The Hague: CONCAWE, 1987.
10. **CONCAWE:** *Economic Consequences of Limiting Benzene/Aromatics in Gasoline* (CONCAWE Report no. 89/57). The Hague: CONCAWE, 1989.
11. **Gallignani, M., S. Garrigues, and M. de la Guardia:** Simultaneous flow analysis fourier transform infrared determination of benzene, toluene, and methyl t-butyl ether in petrol. *Analyst 119*:653–657 (1994).
12. **Hakkola, M., and L. Saarinen:** Exposure of tanker drivers to gasoline and some of its components. *Ann. Occup. Hyg. 40*:1–10 (1996).
13. **CONCAWE:** *A Survey of European Gasoline Qualities—Summer 1990* (CONCAWE Report no. 5/98). Brussels: CONCAWE, 1998.
14. **Vainiotalo, S. Y. Peltonen, A. Ruonakangas, and P. Pfaffli:** Customer exposure to MTBE, TAME, C_6 alkyl methyl ethers, and benzene during gasoline refuelling. *Environ. Health Persp. 107*:133–140 (1999).
15. **Bowden, J.H.:** *Status of Unleaded and Low-Leaded Gasoline Composition* (Contract no. DAAd05-72-C-0053; Interim report FLRL 116:48). Aberdeen Proving Ground, Md.: U.S. Army Coating and Chemical Laboratory, 1972. Cited in "Benzene in gasoline" by H.E. Runion. *Am. Ind. Hyg. Assoc. J. 36*:338–350 (1975).
16. **Runion, H.E:** Benzene in gasoline. *Am. Ind. Hyg. Assoc. J. 36*:338–350 (1975).
17. **National Institute for Occupational Safety and Health (NIOSH):** *Occupational Exposure to Benzene at Service Stations* (NIOSH progress report, June 9, 1976). Cited in *Benzene, Basic and Hazardous Properties* (pp. 117–160) by P.N. Cheremisinoff and A.C. Morresi. New York: M. Dekker, 1979.
18. **U.S. Environmental Protection Agency (EPA):** *Cost of Benzene Reduction in Gasoline to the Petroleum Refining Industry, A.D. Little, Inc. Report to EPA* (EPA publication no. 450/3–78–021), 1978. Cited in *Evaluation of Air Pollution Regulatory Strategies for gasoline marketing industry* (EPA publication no. 450/3–84–012a; pp. 2–3) by EPA. Washington, D.C.: EPA, 1984.
19. **Runion, H.E.:** Benzene in gasoline II. *Am. Ind. Hyg. Assoc. J. 38*: 391–393 (1977).
20. **McDermott, H.J., and G.A. Vos:** Service station attendants' exposure to benzene and gasoline vapors. *Am. Ind. Hyg. Assoc. J. 40*:315–321 (1979).
21. **Tironi, G., and D.G. Hodgkins:** Compliance with the OSHA benzene permissible exposure limit at the gasoline PEL. *Appl. Occup. Environ. Hyg. 6*:881–884 (1991).
22. **Poole, S.K., K.G. Furton, and C.F. Poole:** Determination of benzene and toluene in gasoline by gas chromatography using a liquid organic salt column. *J. Chromatogr. Sci. 26*:67–73 (1988).
23. **Clayton Environmental Consultants, Inc.:** *Gasoline Vapor Exposure Assessment for the American Petroleum Institute (API)* (Clayton project no. 31774.00). Novi, Mich.: Clayton Environmental Consultants, 1991.
24. **Motor Vehicles Manufacturers Association of the United States:** *MVMA National Gasoline Survey, Summer and Winter (1987–1990).* Cited in "Compliance with the OSHA benzene permissible exposure limit at the gasoline PEL" by G. Tironi and D.G. Hodgkins. *Appl. Occup. Environ. Hyg. 6*:881–884 (1991).
25. **Hartle, R.:** Exposure to methyl tert-butyl ether and benzene among service station attendants and operators. *Environ. Health Perspect. 101*(suppl 6):23–26 (1993).
26. **Backer. L.C., G.M. Egeland D. Ashley, et al.:** Exposure to regular gasoline and ethanol oxyfuel during refuelling in Alaska. *Environ. Health Perspectives. 105*:850–855 (1997).
27. **Petroleum Association for Conservation of the Canadian Environment:** A study of exposure to motor gasoline hydrocarbon vapours at service stations. Phase II—summer study (PACE report 87–5). Ottawa, Canada: Petroleum Association for Conservation of the Canadian Environment, 1987.
28. **Petroleum Association for Conservation of the Canadian Environment:** A study of exposure to motor gasoline hydrocarbon vapours at service stations. Phase III—winter study (PACE report 89–3). Ottawa, Canada: Petroleum Association for Conservation of the Canadian Environment, 1989.
29. **Alberta Research Council:** *Canadian Automotive Gasoline—PONAU Analyses.* Ottawa, Canada: The Petroleum Association to Conserve the Canadian Environment, 1991.
30. **Environment Canada:** *Survey of Benzene and Aromatics in Canadian Gasoline—1994* (Report EPS 5/HA/6). Ottawa, Ontario: M. Tushingham Oil, Gas & Energy Division, Environment Canada, 1996.
31. **Environment Canada:** *Survey of Benzene, Aromatics and Olefins in Canadian Gasoline—1998.* Ottawa, Ontario: M. Tushingham. Oil, Gas & Energy Branch, Environment Canada, 1999.
32. **Ikeda, M., M. Kumai, T. Watanable, and H. Fujita:** Aromatic and other contents in automobile gasoline in Japan. *Ind. Health 22*:235–241 (1984).
33. **Foo, S.C.:** Benzene pollution from gasoline usage. *Sci. Tot. Environ. 103*:19–26 (1991).

34. **"Control of Emissions of Hazardous Air Pollutants from Mobile Sources; Proposed Rule."** *Federal Register 65*: 151 (4 August 2000).

35. **U.S. Environmental Protection Agency:** "Control of Emissions of Hazardous Air Pollutants from Mobile Sources." [Online] Available at http://www.epa.gov/orcdizux/regs/ (select toxicpre.pdf).

36. **Urbanus, J.:** "Benzene Content in Gasoline and Crude Oil." October 2000. [Personal Communication] CONCAWE, Boulevard du Souverain 165, B-1160 Brussels, Belgium.

37. **Environment Canada:** "Benzene in Gasoline Regulations." [Online] Available at http://www.ec.gc.ca/oged-dpge/level3e/bzreg/bzrege(projects).htm.