A short primer on benzene, toluene, ethylbenzene and xylenes (BTEX) in the environment and in hydraulic fracturing fluids

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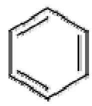
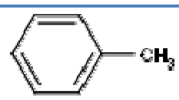
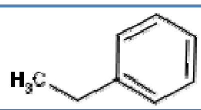
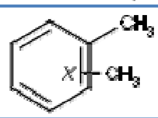
1. Some notes about concentrations

Concentrations in water in this document are generally given as part-per-billion (ppb), equivalent to one microgram per litre (µg/L). A microgram is a millionth of a gram. One ppb is roughly equivalent to a teaspoon of material in an Olympic-size swimming pool. Note that ppb air concentrations cannot simply be converted to $\mu g/m^3$ (and vice versa) but require a conversion factor.

2. What is BTEX?

BTEX is an abbreviation used for four related compounds found in coal tar, crude petroleum and a wide range of petroleum products. The compounds are **B**enzene, **T**oluene, **E**thylbenzene and **X**ylenes.

Table 1. Name, chemical abstract service registry number (CASRN, a unique identifier) and chemical structure of benzene, toluene, ethylbenzene and xylenes (BTEX).

Compound	CASRN	Chemical structure
Benzene	71-43-2	
Toluene	108-88-3	
Ethylbenzene	100-41-4	
Xylenes	1330-20-7	

Once released in the environment, BTEX compounds usually evaporate quickly into the air. BTEX can also dissolve in water, and it may be found in surface and groundwater at contaminated sites or in close vicinity to natural oil, coal and gas deposits.

3. Sources of BTEX

BTEX are naturally-occurring compounds in crude oil. Benzene for example is found at levels up to 4 g/L in crude petroleum, and can be found in sea water (0.8 ppb) in the vicinity of natural gas and petroleum deposits (IPCS 1993). Other natural sources of BTEX compounds include gas emissions from volcanoes and forest fires (IPCS 1985, 1993, 1996, 1997; ATSDR 2007a).

The primary man-made sources of BTEX into the environment are via emissions from motor vehicles and aircraft exhaust, losses during petrol marketing, spills and cigarette smoke. BTEX are created and used during the processing of refined petroleum products and coal and during the production of chemical intermediates and consumer products such as paints and lacquers, thinners, rubber products, adhesives, inks, cosmetics and pharmaceutical products (IPCS 1985, 1993, 1996, 1997; NTP 2005). BTEX compounds are among the most abundantly produced chemicals, with worldwide annual production of 8-10 million tons of benzene (NTP 2005), 5-10 million tons of toluene (ATSDR 2000), 5-10 million tons of ethylbenzene (IPCS 1996) and 10-15 million tons of xylenes (IPCS 1997).

The majority of BTEX released into the environment enter the atmosphere directly. BTEX may be introduced into water by industrial effluents and atmospheric pollution, but releases of BTEX to water are mainly related to spills of petrol and petroleum products or proximity to natural deposits of petroleum and natural gas (IPCS 1985, 1993, 1996, 1997). If present in drinking water sources, BTEX compounds can be efficiently removed by activated carbon filtration (NHMRC 2004).

3.1. BTEX in hydraulic fracturing fluids

BTEX-containing petroleum products (such as diesel) have been used as additives in stimulation fluids, particularly in hydraulic fracturing (fraccing). Well stimulation is used to increase production in oil and gas wells by improving the flow of hydrocarbons into the oil well. Fraccing is the process of pumping high pressure fluids into a coal seam to fracture the seam and allow gas to flow into the gas well, thus maximizing extraction. Fraccing fluid consists mostly of water and sand but small amounts of additives are used to thicken the fluid and improve the efficiency of the process, thus reducing the need for excess water use. The use of BTEX as an additive in fraccing fluids has in the past been permitted in coal seam gas extraction; however since 2003 the US industry has voluntarily agreed to discontinue using BTEX in fraccing fluids due to the availability of safer alternatives (USEPA 2004). In Queensland, BTEX is strictly regulated and must not be used in stimulation fluids in amounts greater than that provided by the legislation (SoQ 2010).

4. Exposure to BTEX

The presence of BTEX in petrol and as a widely used industrial solvent can result in significant and widespread emissions to the environment (Table 2). The most important source of human exposure to BTEX is from breathing of contaminated air, particularly in areas of heavy motor vehicle traffic, petrol stations and through cigarette smoke (IPCS 1985, 1993, 1996, 1997; WHO, 2008). Cigarette smoke in particular can contribute half of the daily exposure to BTEX compounds (ATSDR 2007a). Exposure to BTEX from water contributes only a small percentage of the total daily intake, compared with inhaled air and dietary sources (Table 3).

4.1. Benzene (IPCS 1993, ATSDR 2007a, NTP 2005)

Outdoor environmental levels of benzene range from 0.2 µg/m^3 (0.06 ppb) in remote rural areas to 349 µg/m^3 (107 ppb) in industrial centres with a high density of motor vehicle traffic. The percentage of benzene in unleaded petrol is approximately 1–2%. Driving a motor vehicle one hour per day is estimated to add 40 µg of benzene to a person's daily intake. Levels up to 10,000 µg/m^3 (3,000 ppb) have been measured in air at petrol stations. Spending a little under 2 min/week to refuel a car at the petrol station leads to an additional estimated daily intake of 10 µg. Benzene has been detected at levels as high as 500 µg/m^3 (154 ppb) in indoor residential air. Cigarette smoke contributes significant amounts of benzene to the levels reported in indoor air, with smokers inhaling approximately 1,800 µg benzene/d compared to 50 µg/d by non-smokers. Benzene can also occur in foods and drinks as a product of a reaction between benzoate and ascorbic acid, and has been found in soft drinks in the UK at concentrations as high as 28 ppb (µg/L) (FSA, 2006). In comparison, benzene concentrations in water are generally low (Table 2).

4.2. Toluene (IPCS 1985, ATSDR 2000)

The largest source of toluene release is during the production, transport, and use of petrol, which contains about 5–8% toluene. The concentrations of toluene in air have been found to be quite low in remote areas, but levels of 5-25 µg/m^3 (1.3–6.6 ppb) are common in suburban and urban areas, with levels as high as 1,310 µg/m^3 (350 ppb) in areas of high traffic density. Concentration at petrol station can be as high as 9,000 µg/m^3 (2,400 ppb), and refilling a car can add significantly to daily toluene intake. Toluene is also a common indoor contaminant, being used in common household products such as paints, adhesives and nail polish, as well as from cigarette smoke. Toluene is occasionally detected in drinking water supplies, but occurrence is not widespread and levels are generally below 3 ppb (but can go as high as 3,500 ppb in groundwater from industrially-polluted sites) (Table 2).

4.3. Ethylbenzene (IPCS 1996, ATSDR 2007b)

Ethylbenzene is ubiquitous in ambient air, primarily as a result of industrial releases and vehicle emissions. Petrol contains about 1-2% ethylbenzene. Ethylbenzene concentrations ranging from 0.74 to 360 µg/m^3 (0.1 – 83 ppb) have been measured at urban sites. Levels found at rural sites are generally <2 µg/m^3 (<0.46 ppb). Ethylbenzene releases to the air especially in indoor environments can occur with the use of consumer products such as pesticides, liquid process photocopiers and plotters, solvents, carpet glue, paints, varnishes, automotive products, adhesives, and fabric and leather treatments that contain ethylbenzene. Ethylbenzene is detected infrequently in drinking water (Table 2). Ethylbenzene levels in uncontaminated groundwater are generally <0.1 ppb. However, much higher levels have been reported for groundwater contaminated via waste disposal, fuel spillage and industrial facilities. At a solvent recovery facility, ethylbenzene concentrations of up to 28,000 ppb were measured in contaminated groundwater.

4.4. Xylenes (IPCS 1997, ATSDR 2007c)

Xylene is primarily released from industrial sources, in motor vehicle exhaust (petrol contains 7-10% xylenes), and during its use as a solvent. Typically, background levels of xylene in ambient air are around 1 µg/m^3 (0.23 ppb), but in suburban areas it is around 3 µg/m^3 (0.69 ppb). Higher levels have been measured in urban and industrialized areas, up to 775 µg/m^3 (178 ppb). In some cases, indoor levels of xylene can be higher than outdoor levels, especially in buildings with poor ventilation. Typically, background levels of xylenes in surface and ground waters are low (<0.1 ppb) (Table 2). Much higher levels have been measured in some industrial areas and areas associated with the oil industry.

Table 2. Reported concentrations of benzene, toluene, ethylbenzene and xylene (BTEX) in air and water.

	Benzene	Toluene	Ethylbenzene	Xylenes
Air (µg/m^3)				
Remote rural area	0.2 – 16	0.5 – 260	0.2 – 1.6	<0.1 – 3
Industrial centre with high traffic density	Up to 349	Up to 1,310	Up to 360	Up to 775
Water (ppb or µg/L)				
Surface water	<0.1 – 2.1	<1 – 15	<0.1 – 1.8	<0.1 – 1.2
Contaminated surface water	Up to 100	NA	Up to 15	Up to 32
Groundwater	<0.1 – 1.8	<1 - 100	<0.1 – 1.1	<0.1 – 0.5
Contaminated groundwater	Up to 330	Up to 3,500	Up to 2,000	Up to 1,340
Drinking water	<0.1 – 5	<1 – 27	<1 - 10	<0.1 – 12

Notes: All data in this table from ATSDR 2000, 2007a, 2007b and 2007c; IPCS 1985, 1993, 1996 and 1997; NTP 2005; WHO 2008; and NHMRC 2004.

Table 3. Estimated daily intakes of benzene, toluene, ethylbenzene and xylenes (BTEX). All values are in all in µg/d.

	Benzene	Toluene	Ethylbenzene	Xylenes
Air breathing	90 – 1,300	2 – 12,000	2 – 3,600	70 – 2,000
Cigarette smoking	1,800	2,000	40[a]	Up to 190[a]
Food	Up to 250	Up to 64	NA	NA
Drinking water	Up to 10[b]	Up to 43	Up to 20[b]	Up to 24[b]

Notes: Unless otherwise indicated, all data in this table from ATSDR 2000, 2007a, 2007b and 2007c; IPCS 1985, 1993, 1996 and 1997; NTP 2005; WHO 2008; and NHMRC 2004. [a] Assuming 5 cigarettes/d; [b] Assuming 2 L/d. NA: Not applicable.

4.5. Exposure to BTEX from hydraulic fracturing

There are two potential exposure sources to BTEX from hydraulic fracturing: 1) use of BTEX in fraccing fluids, and 2) fracturing through hydrologic confining layer and creating of a hydraulic communication between the coal seam and underground aquifers used for groundwater.

A report by the US Environmental Protection Agency (USEPA) showed that if BTEX was used as an additive to fraccing fluids, the concentration of BTEX at the point of injection would be 45-4,400 ppb for benzene, 120-31,000 ppb for toluene, 120-8,700 ppb for ethylbenzene and 330-26,000 ppb for xylenes (USEPA 2004). The report concluded that while these concentrations were high, the risk of contaminating groundwater sources of drinking water was minimal due to recovery of injected fluids (68-82%) combined with the mitigating effects of dilution and dispersion, adsorption and biodegradation (USEPA 2004).

BTEX are natural compounds found in crude oil, coal and gas deposits. As such, they may be naturally present at low concentrations in groundwater abstracted from aquifers in the vicinity of these deposits, whether BTEX has been used in fraccing fluids or not. Hydraulic fracturing may cause a link between BTEX-rich coal seam and nearby groundwater. The extent and nature of these fractures depend on the depth of the fracturing process and the local geomorphology. After careful modelling and evaluation, the USEPA report concludes that the possible hydraulic connections are unlikely to represent a significant potential threat to drinking water sourced from groundwater (USEPA 2004).

5. Impacts of exposure to BTEX

5.1. In humans

After exposure to BTEX, several factors determine whether harmful health effects will occur, as well as the type and severity of such health effects. These factors include the amount of BTEX to which you are exposed and the length of time of the exposure, as well as which BTEX compound you were exposed to. Of the four BTEX compounds, benzene is the most toxic. Most toxicity data is available for airborne exposure to BTEX, as this is the most common route of exposure to these volatile compounds.

Benzene is rapidly and efficiently absorbed and widely distributed throughout the body. Exposure to very high concentrations in air (10,000,000 ppb and above) can cause death (ATSDR 2007a). Lower levels (700,000 – 3,000,000 ppb) can cause drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness. Long term exposure to benzene can cause cancer of blood forming organs (leukaemia). Eating foods or drinking liquids containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, rapid heart rate, coma, and death. The health effects that may result from eating foods or drinking liquids containing lower levels of benzene are not known (ATSDR 2007a).

Toluene is readily absorbed from the gastrointestinal tract after ingestion, and is distributed preferentially in adipose tissue, then the kidneys, liver and brain. The main effect of toluene is on the brain and nervous system, with fatigue and drowsiness being the most obvious symptoms (ATSDR 2000).

Ethylbenzene is readily absorbed from the human gastrointestinal tract. Animal studies show enlargement of the liver and kidney at high doses (400 mg/kg body weight per day). Liver effects were also observed in a number of inhalation studies. In general, acute and chronic toxicity is low in humans although symptoms such as irritation of eyes and the respiratory tract have been reported at high levels of exposure in air (IPCS 1996). Exposure to relatively low concentrations of ethylbenzene for several days to weeks resulted in potentially irreversible damage to the inner ear and hearing of animals (ATSDR 2007b).

Xylenes are readily absorbed after inhalation. Both short- and long-term exposure to high concentrations of xylene can also cause a number of effects on the nervous system, such as headaches, lack of muscle coordination, dizziness, confusion, and changes in one's sense of balance as well as irritate the eyes and respiratory tract (ATSDR 2007c, IPCS 1997).

5.2. In aquatic organisms

Toxicity testing for BTEX compounds have also been conducted on aquatic organisms. Typically water concentrations in excess of 1 mg/L are required to produce acute toxic effects in organisms such as algae, daphnids and fish. Due to low background concentrations of these chemicals in water, rapid volatilization and degradation processes and their low to moderate toxicity, the overall risk to the aquatic environment is therefore considered low. It should be noted, however, that higher concentrations of these chemicals can occur in water at contaminated sites (IPCS 1985, 1996, 1997, USEPA 2010).

6. Guideline BTEX levels

6.1. Water

Public health guidelines for BTEX are available for drinking water in the Australian Drinking Water Guidelines (ADWG; NHMRC 2004). In air, different types of guidelines are available for both ambient and occupational settings (Air Toxics NEPM; EPHC 2004).

Benzene is a known carcinogen (cancer causing). The ADWG specify that it should not be detected in drinking water. For practical reasons, the drinking water guideline for benzene is 1 ppb (which is the analytical detection limit) (NHMRC 2004). The remaining chemicals (toluene, ethylbenzene and xylenes) are not recognized as carcinogenic (IARC 1989) and their drinking water guidelines are much higher (Table 4).

It is important to understand that health guidelines (such as the ADWG) are based on an acceptable daily intake. This is the amount of a chemical that can be ingested every day over a lifetime without adverse effect. Drinking water guidelines are set according to an acceptable daily intake based on a 70 kg person drinking 2 litres of water every day for 70 years. These guidelines provide a significant margin of safety – for example most people do not drink 2 litres of water per day and they are not constantly exposed to guideline levels of contaminants in their drinking water supply. This means that short-term exceedance of the guidelines do not necessarily represent a significant health risk depending on how often and how long these exceedances occur (enHealth 2002).

The following table summarizes current Australian and selected international guidelines both for drinking and environmental waters for the four components of BTEX.

Table 4. Water guidelines for benzene, toluene, ethylbenzene and xylene (BTEX). All values are in ppb (µg/L).

	CASRN[1]	QPHR[2]	ADWG[3]	WHO DWG[4]	US NPDWS[5]	ANZECC (99% protection)[6]
Benzene	71-43-2	1	1	10	5	600
Toluene	108-88-3	800	800 (25 for aesthetics)*	700	1 000	180
Ethylbenzene	100-41-4	300	300 (3 for aesthetics)*	300	700	50
Xylene	1330-20-7	600	600 (20 for aesthetics)*	500	10 000 (total xylenes)	200

[1] Chemical Abstract Services Registry Number; [2] Queensland Public Health Regulation (QHPR 2005); [3] Australian Drinking Water Guidelines (NHMRC 2004); [4] World Health Organisation Drinking Water Guidelines (WHO 2008); [5] United States National Primary Drinking Water Standards (USEPA 2003); [6] Australian and New Zealand Environment Conservation Council Environmental Protection Guidelines (ANZECC 2000). * Toluene, ethylbenzene and xylenes have a lower aesthetics guidelines than a health guideline. This is because these compounds will be noticeable by smell or taste before they become a health risk.

6.2. Air

The National Environment Protection (Air Toxics) Measure (Air Toxics NEPM) provides a framework for monitoring, assessing and reporting on ambient levels of five air toxics that includes benzene, toluene and xylene to assist in the future development of national air quality standards for these pollutants. The Air Toxics NEPM uses the term 'monitoring investigation levels' for air toxics. If these levels are exceeded then further investigation may be appropriate, but exceedance does not indicate that adverse health effects will occur and the goal is to gather sufficient data nationally to facilitate development of standards. As with the drinking water guidelines, benzene has the lowest value at 3 ppb (Table 5).

In Queensland, the Environmental Protection (Air) Policy 2008 (SoQ 2008) specifies guidelines for benzene, toluene and xylenes in air to ensure protection of human and environmental health from those pollutants in air (Table 5). The guidelines levels are based on the Air Toxics NEPM investigations levels.

Table 5. Air quality guidelines for benzene, toluene, ethylbenzene and xylene (BTEX). All values are in ppb.

	CASRN	NEPM Air Toxics (Annual Average)	Queensland (Air) EPP (Annual Average)
Benzene	71-43-2	3	3
Toluene	108-88-3	100	100 [a]
Ethylbenzene	100-41-4	NA	NA
Xylene	1330-20-7	200	200 [b]

Notes: [a] with concentrations up to 1,000 ppb acceptable for up to 24h. [b] with concentrations up to 250 ppb acceptable for up to 24h. NA: Not applicable

7. Conclusions

The primary exposure to BTEX is from breathing air contaminated by motor vehicle emissions, industrial use and cigarette smoke. The levels in drinking water are usually very low and intake from drinking and food sources is usually minor in comparison. However, contamination from fuel spillage and industrial activities can result in localised high concentrations in surface and groundwater. In those instances, activated carbon filtration is an effective treatment option to reduce BTEX concentrations to acceptable levels.

Use of BTEX in fraccing fluids is currently out of favour due to the availability of safer alternatives. Nevertheless, if BTEX were used in fraccing fluids, it is unlikely to significantly contribute to contamination of drinking water from groundwater sources. Groundwater in the vicinity of natural oil, gas and coal deposits may however contain elevated levels of naturally-occurring BTEX compounds. The local geomorphology and possibility of creating hydraulic connections between coal seam and nearby groundwater must be taken into account prior to using hydraulic fracturing.

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