Supplementary Paper: Additional information about potential pollutants and toxins

Introduction

All industrial activity, including transportation, industrial agriculture, and waste disposal activities, lead to pollution, through the introduction of harmful substances into the environment. These contaminate air, water, soil and are taken up by living organisms. Human exposure then occurs through inhalation and through ingestion either directly or via food. Exposure for industrial workers is managed and minimised through measures such as protective garments and masks, careful monitoring, and procedures that ensure minimum exposure. Our understanding of the harms caused by pollution is increasing all the time, partly helped by advances in epidemiological methods. The Committee on the Medical Effects of Air Pollution (COMEAP) has worked on quantifying the effects of air pollution, leading to an understanding that long term exposure even to low levels of pollutants does cause significant premature illness and deaths, with heart disease being the biggest single impact.

Shale gas extraction, like all industrial activity, will inevitably add to the burden of poor air quality and to the contamination of water, earth and ecosystems. This appendix lists some of the key pollutants involved, and summarises some of the key characteristics of these substances.

BTEX is an acronym that stands for benzene, toluene, ethylbenzene, and xylenes. These are a group of volatile organic compounds (VOCs) that are located within the shale and which can be released by fracking along numerous points of the shale gas production system. They form part of the fugitive emissions and they contaminate the flowback and other waste water produced at drilling sites. The BTEX compounds can evaporate from the flowback and waste water and remain in the air for several days. They are also found in petroleum derivatives such as gasoline and are released in diesel fumes.

Fracking sites therefore present multiple sources and exposure routes for *BTEX*: from the ground and above it. BTEX compounds may contaminate the soil and groundwater at hydraulic fracturing sites and in the areas with storage tanks.[1] They can be present in the air. The main route of exposure for humans is via inhalation i.e. vapour in ambient air. Ingestion (contaminated water) and dermal exposure (e.g. direct skin contact with fuels and solvents) are less common routes of exposure.

Factors known to influence the air concentrations of benzene and other VOCs include the temperature and pressure of the process liquids and conditions in the hydrocarbonreservoir , as well

[1] Gross SA *et al* Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations *Journal of the Air & Waste Management Association* Volume 63, Issue 4, 2013

as the ambient air temperature.[2] There are likely to be other, as yet undetermined, influencing factors.

Benzene is one of the constituents of BTEX and is of particular concern due to its toxicity to humans. It occurs naturally in crude oil and hydrocarbon fuels. Benzene is a recognised carcinogen and is a known risk factor for various forms of leukaemia, even at low levels of exposure. Immediate health impacts range from irritation of eyes, nose, mouth, and throat to aggravated asthma and other respiratory conditions. Acute exposure to relatively high concentrations of benzene causes central nervous system disturbances consistent with solvent exposure; drowsiness, dizziness, headache, tremor, delirium, ataxia, loss of consciousness, respiratory arrest and death. [3 4 5 6]

Benzene exposures have also been implicated in neurological disorders, immune dysfunction and neural tube birth defects (NTDs) including spina bifida.[7] Men exposed to benzene are more likely to have aneuploidy, an abnormal amount of chromosomes, in their sperm, which may impact fertility and fetal development.[8] Preliminary studies have also suggested that benzene exposure may increase the risk of birth defects including neural tube defects and congenital heart defects found in populations living near hydraulic fracturing sites.[9]

Benzene was among the first pollutants found in air samples near shale gas operations. In a recent study, the US Centers for Disease Control and Prevention (CDC) reported alarmingly high benzene metabolite concentrations in the urine of workers at a fracking site.[10] A study commissioned by the West Virginia Department of Environmental Protection found that, at many hydraulic fracturing sites, benzene concentrations above levels considered to be *"the minimum risk level for no health*

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[2] Lagario S *et al* Exposure to benzene and childhood leukaemia: a pilot case-control study[1], *BMJ Open* 2013;3:e002275 doi:10.1136/bmjopen-2012-002275

[3] Health Protection Agency Benzene Toxicological Overview RP Chilcott CRCE HQ, HPA 2011, Version 4

[4] Glass DC *et al* **Leukemia** Risk Associated with Low-Level **Benzene** Exposure *Epidemiology,* 9/1/2003, Vol. 14, Issue 5, p. 569-577

[5] Zhou Y *et al* Maternal **Benzene** Exposure during Pregnancy and Risk of Childhood Acute Lymphoblastic **Leukemia**: A Meta-Analysis of Epidemiologic Studies.], ISSN: 1932-6203, *Plos One (PLoS One)*2014 Oct 15; Vol. 9 (10), pp. e110466.

[6] Schnatter AR, 2012. Myelodysplastic Syndrome and Benzene Exposure Among Petroleum Workers: An International Pooled Analysis *JNCI J Natl Cancer Inst* 104 (22): 1724-1737.
Vlaanderen, J *et al* Flexible Meta-Regression to Assess the Shape of the **Benzene—Leukemia** Exposure—Response Curve *Environmental Health Perspectives,* 2010, Vol. 118, Issue 4, 526-532
Lan Q *et al* Hematotoxicity in in workers exposed to low levels of benzene Science 306 1774-17
Cogliano VJ *et al*, Preventable Exposures Associated With Human Cancers *JNCI J Natl Cancer Inst* (2011) 103 (24): 1827-1839.

[7] Lupo PJ *et al* 2010. **Maternal exposure to ambient levels of benzene and neural tube defect among off-spring, Texas, 1999-2004.** *Environmental Health Perspectives* volume 119 | number 3 | March 2011 307-402

[8] *Xing C et al* Benzene Exposure Near the U.S. Permissible Limit Is Associated with Sperm Aneuploidy *Environmental Health Perspectives* • volume 118 | number 6 | June 2010 833-839.

[9] McKenzie LM, Birth Outcomes and Maternal Residential Proximity to Natural Gas Development in Rural Colorado *Environ Health Perspect*; volume 122 | number 4 | April 2014 412-417

[10] Esswein EJ *et al,* Evaluation of Some Potential Chemical Exposure Risks During Flowback Operations in Unconventional Oil and Gas Extraction: Preliminary Results *Journal of Occupational and Environmental Hygiene* (2014) **11** (10) p.D174-D184

effects" by the CDC were found 625 feet away from oil and gas activity.[11] Benzene emissions in the air near rural fracking sites have also been detected in several other recent independent studies at previously unsuspected and dangerously high levels, which even exceed those reported from the most heavily polluted inner cities.[12] [13]

Because benzene air concentrations in and around fracking sites are so unpredictable, and have such dynamic spatial and temporal variability, it may never be possible to control or regulate these emissions. A preliminary US study has suggested that benzene may be the largest contributor to excess lifetime cancer risk within a half mile from fracking sites.[14] Therefore, in order to protect the public, any unnecessary exposures to benzene should be avoided.[15]

A health risk assessment in Colorado's heavily drilled Garfield County identified many hydrocarbon pollutants associated with adverse respiratory and neurological effects and also found that concentrations of BTEX increased with proximity to the well site and were up to nine times higher during well completion than during well production. In tight gas fields[16] in rural north-eastern Utah, researchers estimated the total annual mass flux of VOCs from the surveyed gas fields to be equivalent to the emissions from 100 million cars. The benzene levels measured in this study also exceeded health standards set by the ATSDR and California Environmental Protection Agency to prevent harm to the developing foetus, immune system and blood.[17]

Another recent study found elevated concentrations of potentially dangerous chemicals near fracking sites in the USA including significant concentrations of four toxic chemicals: benzene, formaldehyde, hexane and hydrogen sulphide, with concentrations of benzene exceeding health-based risk levels by several orders of magnitude (some monitors detected benzene at higher

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[11] West Virginia Department of Environmental Protection, Division of Air Quality, "*Air, Noise, and Light Monitoring Results For Assessing Environmental Impacts of Horizontal Gas Well Drilling Operations (ETD - 10 Project)*," Charleston, WV.

[12] Petron g *et al;* Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study *Journal of Geophysical Research: Atmospheres* Volume 117, Issue D4, 27 February 2012, 1-19.

[13] Helmig D *et al*, Highly Elevated Atmospheric Levels of Volatile Organic Compounds in the Uintah Basin,Utah. *Environ. Sci. Technol.*, 2014, ***48*** (9), pp 4707–4715

[14] McKenzie' , LM et al Human health risk assessment of air emissions from development of unconventional natural gas resources *Science of The Total Environment* Volume 424, 1 May 2012, Pages 79–87

[15] The HSE (UK) Workplace Exposure Limit Guideline is set at 1 part of benzene per million parts of air, 1 ppm or 3.25 mg/m -3 in the workplace during an 8-hour workday.[15] The short term exposure limit for airborne benzene is 5 ppm for 15 minutes. These legal limits were based on studies demonstrating compelling evidence of health risk to workers exposed to benzene. The risk from exposure to 1 ppm for a working lifetime has been estimated as 5 excess leukemia deaths per 1,000 employees exposed. (REF: HSE Workplace Exposure Limits Guideline 2007)

[16] Tight gas is a term used to describe natural gas that is dispersed within low-porosity silt or sand - in contrast to shale gas which is trapped in rock. Similar technology is used to access and extract tight gas.

[17] Helmig D, Thompson CR, Evans J, *et al,* 2014. Highly Elevated Atmospheric Levels of Volatile Organic Compounds in the Uintah Basin, Utah. *Environmental Science & Technology*, 48 (9): 4707–4715; **DOI:** 10.1021/es405046r

concentrations than anything found in the published literature).[18] High benzene concentrations were detected at residential property up to 350 yards from the nearest fracking site, and on farmland along the perimeter of a well pad. High concentrations of benzene were found in the air up to 885 feet from fracking well-heads.

Toluene Is another BTEX constituent, chronic exposure to which is is linked to liver, kidney, neurological damage and effects on the reproductive system. Local effects following inhalation include irritation to the nose, throat and respiratory tract. Severe acute inhalation can cause bronchospasm and pulmonary oedema as well as central nervous system toxicity and cardiac arrhythmias.[19]

Ethylbenzene is of less concern, although it can have some toxic effect.

Xylene exposure can cause irritation to the mouth, nose, throat and lungs if inhaled or ingested. Other symptoms include dizziness and headache and confusion, and high levels of exposure can cause cardiac, liver and kidney damage.[20]

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Formaldehyde is another toxic substance that is of concern in relation to fracking. It is a gas at room temperature, and has a characteristic pungent, irritating odor. Elevated levels of formaldehyde have been found near shale gas operations in several states.[22] [23] Formaldehyde levels as low as 0.046 ppm are positively correlated with eye and nasal irritation. A review of studies has shown a strong association between exposure to formaldehyde and the development of childhood asthma.[24] Chronic exposure at higher levels, starting at around 1.9 ppm, has been demonstrated to result in significant damage to lung function,.[25] Formaldehyde causes a range of other adverse health effects

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[18] Macey GP *et al,* Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. *Environmental Health (*2014) **13**: 82; doi:10.1186/1476-069X-13-82.
[19] Health Protection Agency: *Toluene Toxicological Overview* K Foxall CHAPD HQ, HPA 2007 Version 1
[20] Health Protection Agency Xylene K Foxall CRCE HQ, HPA 2010 Version1
[21] Health Protection Agency: *Toluene Toxicological Overview* K Foxall CHAPD HQ, HPA 2007 Version 1
[22] Macey GP *et al* 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. *Environmental Health*13:82;doi:10.1186/1476-069X-13-82
[23] Shonkoff SB, Hays J, Finkel ML. 2014. Environmental Public Health Dimensions of Shale and Tight Gas Development. Environmental Health Perspectives 122; doi:10.1289/ehp.1307866.
[24] McGwin G *et al* Formaldehyde Exposure and Asthma in Children: A Systematic Review *Environ Health Perspect.* 2010 March; 118(3): 313–317.
[25] Tang X *et al* Formaldehyde in China: Production, Consumption, Exposure Levels, and Health Effects. *Environmental International*. 2009. 35 (8) 1210–1224

including acute mucus membrane irritation, eczema and reproductive toxicity.[26] [27] In addition, it has now been classified in the US as a known human carcinogen based on animal and human studies.[28] Increased leukaemia rates have also been observed in some studies of anatomists, pathologist and embalmers who often have formaldehyde exposure, but no consistent evidence of increased leukemia rates has been found in industrial workers. A 2012 UK review concluded that there is 'strong' but not sufficient evidence for a causal association between leukaemia and occupational exposure to formaldehyde.[29]

Radon is a naturally occurring colourless and odourless gas that emits radioactivity. Exposure to high concentrations of radon leads to an increased risk of lung cancer. The report by Public Health England concluded that any potential exposure to radon would be at very low levels, although they qualified this by saying that "it would be worth reviewing the existing radiological assessment of radon in natural gas against the parameters that might apply to shale gas extraction for reassurance purposes" and that "it would be useful to have an improved evidence base of relevant field measurements" in the case of potential radon contamination of water.

Hydrogen sulphide is an important occupational hazard in shale gas extraction and requires a high standard of health and safety in order to protect workers. The impacts for the general population are probably less significant, but in highly populated areas this could be an issue of concern to the public. Hydrogen sulphide (H_2S) is a colourless flammable gas with the characteristic odour of rotten eggs, andis produced both naturally during the decay of plant and animal proteins, and through human activity. It can be found in natural gas and the extraction of natural gas may release significant air concentrations of H_2S. A recent survey in Texas reported that thirty-two shale gas sites (8.0%) had H_2S concentrations > 4.7 parts per billion, well above the odour recognition threshold, beyond the perimeter fence line.[30] Occupational exposure is known to occur in the shale gas industry and many companies routinely require the use of personal H_2S monitors and H_2S training programs.

H_2S is considered a broad-spectrum toxin, meaning that it can poison several different systems in the body, although the nervous system is most affected. It's toxicity is comparable with that of hydrogen cyanide or carbon monoxide. It forms a complex bond with iron in the mitochondrial cytochrome enzymes, thus preventing cellular respiration. At some threshold level, believed to average around 300–350 ppm, the oxidative enzymes become overwhelmed. Death may occur from the second

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[26] Kim K-H *et al* 2011. Exposure to Formaldehyde and Its Potential Human Health Hazards. *Journal of Environmental Science and Health,* Part C 29:277–299; doi:10.1080/10590501.2011.629972

[27] Duong A *et al* Reproductive and developmental toxicity of formaldehyde: A systematic review *Mutation Research/Reviews in Mutation Research* Volume 728, Issue 3, November–December 2011, 118–138

[28] **U.S. Department of Health and Human Services** *13th Report on Carcinogens* on October 2, 2014

[29] The Burden of occupational cancer in Great Britain: Leukaemia. Prepared by the Health & Safety Laboratory, the Institute of Occupational Medicine and Imperial College London for the Health & Safety Executive 2012: RR856

[30] Eapi GR *et al* Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. *Journal of the Air & Waste Management Association* (2014) Volume 64, Issue 8, 927-944

inhalation of the gas. In 1975, a H_2S release from an oil drilling operation in Denver City, killed nine people and caused the Texas state legislature to focus on the deadly hazards of the gas.[31] However current data from the USA regarding the frequency of exposure to H_2S or resulting deaths in gas and oil extraction worksites are not available.

Being heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. Although very pungent at first, it quickly deadens the sense of smell, so victims may be unaware of its presence until it is too late. Exposures during shale gas operations can occur during well servicing, tank gauging and swabbing operations.

If death does not occur, high exposure to H_2S can lead to serious impacts on the central nervous system including cortical pseudolaminar necrosis, degeneration of the basal ganglia and cerebral oedema. Although respiratory paralysis may be immediate, it can also be delayed up to 72 hours. At low concentrations, local inflammation is believed to be caused by H_2S. Skin exposure may cause discolouration, pain, itching and erythema. Eye exposure may cause irritation, inflammation, tearing, sensitivity to light and conjunctivitis. Respiratory exposure commonly causes nose-bleeds, sore throat, and cough which may progress to pulmonary oedema and shortness of breath.[32] Since H_2S occurs naturally in the body, the environment and the gut, enzymes exist in the body capable of detoxifying it by oxidation to harmless sulphate. Hence very low levels of H_2S may be tolerated indefinitely. However, long-term low-level exposure may result in fatigue, loss of appetite, headaches, irritability, poor memory, and dizziness.[33]

Diesel exhaust emissions

The International Agency for Research on Cancer (Volume 105 of the IARC Monographs) 2012 Working Group has concluded that there is sufficient evidence in humans for the designation of diesel exhaust emissions as Group 1 carcinogens. Several influential epidemiological studies, adjusting for tobacco smoking, support a causal association between exposure to diesel-engine exhaust and lung cancer.[34]

Fine particulate matter (PM)

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[31] Witter RZ *et al* Occupational exposures in the oil and gas extraction industry: State of the science and research recommendations *American Journal of Industrial Medicine* Volume57,Issue7, 2014 Pages 847–856

[32] Mousa HAL, Short-term effects of subchronic low-level hydrogen sulphide exposure on oil field workers Environmental health and preventive medicine (2015) 20:12-17

[33] Public Health England: Hydrogen Sulphide General Information, Prepared by Toxicology Department CRCE, PHE, 2009, Version 1

[34] Benbrahim-Tallaa L *et al* Carcinogenicity of diesel-engine and gasoline-engine exhausts and some nitroarenes *The Lancet Oncology* Volume 13, No. 7, p663–664, July 2012

Fine particulate matter ($PM_{2.5}$) can lodge deep within the lungs and enter the systemic circulation increasing the risk of asthma attacks, cardiopulmonary disease and respiratory disease; and is a known risk factor associated with premature mortality.[35] There are also known associations between short-term exposure to $PM_{2.5}$ and adverse health outcomes. A recent report of a small but statistically significant association between impaired lung function and increased exposure to micro-particulate air pollution, could have implications for individuals with chronic respiratory disease living near hydraulic fracturing sites.[36] Moreover, exposure to $PM_{2.5}$ originating from outdoor sources of diesel is associated with exacerbation of asthma in children, especially in the winter.[37]

[35] Atkinson RW, *et al.* Epidemiological time series studies of PM2.5 and daily mortality and hospital admissions: a systematic review and meta-analysis *Thorax* 2014;0:1–6

[36] Molter A *et al* Long-term exposure to PM10 and NO2 in association with lung volume and airway resistance in the MAAS cohort. Environmental Health Perspectives (2013) 121, (10): 1232-1236.

37 Habre R et al The effects of $PM_{2.5}$ and its components from indoor and outdoor sources on cough and wheeze symptoms in asthmatic children *Journal of Exposure Science and Environmental Epidemiology* 24, 380-387 (July/August 2014)