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Toxic Chemicals in Unconventional Gas Exploration and Production [1]

'UG exploitation and production may have unavoidable environmental impacts. Some risks result if the technology is not used adequately, but others will occur despite proper use of technology. UG production has the potential to generate considerable GHG emissions, can strain water resources, result in water contamination, may have negative impacts on public health (through air and soil contaminants; noise pollution), on biodiversity (through land clearance), food supply (through competition for land and water resources), as well as on soil (pollution, crusting).' [2]

- UNEP Global Environmental Alert System 2012

Unconventional Gas (UG) refers to natural gas from unconventional sources such as shale deposits, coal seams, tight sandstones and methane hydrates. Natural gas consists primarily of methane with other hydrocarbons, carbon dioxide, nitrogen and hydrogen sulfide.

Shale gas is found in natural shale fractures and in the pore spaces. Shale has low permeability and must be hydraulically fractured to release the gas. Approximately 7.7 - 38 megalitres (2-10 million gallons) of water mixed with various chemical and physical additives is needed to complete each fracturing of a horizontal well.

Coal seam gas or coal bed methane is natural gas adsorbed into the coal. To release the gas, the coal seam must be depressurised by pumping the water to the surface. As the pressure within the coal seam declines hydraulic fracturing is used. The US EPA estimate 0.2 - 1.3 megalitres (50,000 to 350,000 gallons) of water is required for each hydraulic fracturing of a CSG well. Shale gas reservoirs are typically found at 2,000 to 2,300 metres below ground, deeper than coal bed methane reservoirs, which are situated at 800 to 1,200 metres. The closer the gas reservoirs are to ground water aquifers the greater the chance of hydraulic communication with that aquifer and resultant water contamination.

Chemical Use - Unconventional gas activities use large quantities of chemical additives in drilling and hydraulic fracturing fluids. The mixtures are unassessed for toxicity or persistence and can also form new compounds when exposed to sunlight, water, air, radioactive elements or other natural chemical catalysts.

Hydraulic fracturing *(fracking)* involves injecting wells at high pressure with water, proppants, radioactive tracers and large quantities (eg 18,500 kilograms[3]) of chemical additives to fracture the formation and produce new cracks and pathways to help extract the gas. Up to 40% of the chemical additives may not be recovered.[4] A well can be 'fracked' a number of times. The US House of Representatives Committee on Energy and Commerce[5] identified over 750 chemical products, with 650 containing hazardous substances and 279 products including trade secrets were identified. These include carcinogens (eg naphthalene),

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[1] Adapted from NTN presentation *Unconventional Gas: Shared Environmental Health Concerns* presented to the OECD Focus Session on Chemicals Used and Released in Hydraulic Fracturing, Paris, November 2012 by Dr Mariann Lloyd-Smith, Senior Advisor, National Toxics Network Inc. / IPEN

[2] UNEP Global Environmental Alert system Gas fracking: can we safely squeeze the rocks? http://na.unep.net/api/geas/articles/getArticleHtmlWithArticleIDScript.php?article_id=93

[3] Coal Seam Hydraulic Fracturing Fluid Risk Assessment. Response to the Coordinator-General Requirements for Coal Seam Gas Operations in the Surat and Bowen Basins, Queensland. Golder Associates 21 October 2010

[4] ibid

[5] United States House of Representatives Committee on Energy and Commerce, Minority Staff, April 2011 Chemicals Used In Hydraulic Fracturing. http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf

neurotoxins (eg isopropanol*),* irritants/sensitisers (eg sodium persulfate*)*, reproductive toxins (eg ethylene glycol) and endocrine disruptors (eg nonylphenol).

Industry self-reporting on 9,310 individual fracking operations conducted in the US between January 2011 and September 2012, noted cancer causing chemicals were used in one out of every three hydraulic fracturing operations. While not all companies report and not all chemicals used in the process are disclosed because of 'trade secret' exemptions, industry did report that known carcinogens like naphthalene, benzyl chloride and formaldehyde were used in 34 percent of all fracking operations.[6] In Australia, the vast majority of fracking chemicals have not been formally assessed. Of the 23 identified as commonly used 'fracking' chemicals, only 2 had been assessed by the national regulator, National Industrial Chemicals Notification and Assessment Scheme (NICNAS) and neither was for their use in CSG.[7]

Proppants (eg 40-50,000 kg) consisting of silica or manufactured ceramic polymer spheres based on alumino-silicates are injected as part of the fracturing fluid mixture and remain in the formation to hold open the fractures once the pressure is released. Breathing silica can cause silicosis, and exposure to silica dust is a known cause of lung cancer and a suspected contributor to autoimmune diseases, chronic obstructive pulmonary disease and chronic kidney disease.[8] According to Haliburton's patent[9] acrylic polymers consisting of 85% acrylonitrile, a human carcinogen are used for proppant spheres. Acrylonitrile has been detected in US air sampling of gas sites at high levels.

Flowback refers to the 15 - 80% of the hydraulic fluid mixture that returns to the surface. It contains some of the chemicals injected, plus contaminants from the coal seam like BTEX, PAHs, naturally occurring radioactive materials (NORMs), heavy metals and other volatile organic compounds (VOCs). Samples taken from the top of the well-head, a day after the well had been 'fracked', demonstrated the presence of the VOCs; bromodichloromethane, bromoform, chloroform and dibromochloromethane, as well as benzene and chromium, copper, nickel, zinc.[10]

Produced water is the term used by the industry to describe the waste water produced along with the gas. Produced water from both CSG and shale gas is contaminated with heavy metals, NORMs, fracking or drilling chemicals, volatile and semi volatile organic compounds and high concentrations of salts. For a typical shale gas well, daily produced water volumes range from 300 – 4,500 litres (80 to 1,200 gallons). The amount of produced water from a CSG well varies between 0.1 - 0.8 ML per day. Produced water is either re-injected into aquifer formations, used for dust suppression on roads, reused for brick making, sent to holding ponds or partially 'treated' and released into waterways. The treatments to remove contaminants from produced water are limited by the chemicals they can remove, the energy needed and their economic costs. Reverse osmosis filtration has significant limitations and cannot remove many of the organic chemicals used in UG activities.[11] Low molecular weight, non polar, water soluble solutes such as the methanol and ethylene glycol are poorly rejected.[12]

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[6] http://ecowatch.org/2013/cancer-causing-chemicals-fracking-operations/

[7] Lloyd-Smith, M.M & Senjen, Rye, Hydraulic Fracturing in Coal Seam Gas Mining: The Risks to Our Health, Communities, Environment and Climate, National Toxics Network September 2011 Available www.ntn.org.au

[8] NIOSH Hazard Review, Health Effects of Occupational Exposure to Respirable Crystalline Silica. National Toxicology Program [2012]. Report on carcinogens 12th ed. U.S. Department of Health and Human Services, Public Health Service. See www.osha.gov/dts/hazardalerts/hydraulic_frac_hazard_alert.htm

[9] Halliburton Patent 7799744, Polymer-Coated-Particulates, www.docstoc.com/docs/58860687/Polymer-Coated-Particulates---Patent-7799744

[10] Halogenated Contaminants From Coal Seam Gas Activities Lloyd-Smith M [1]*, Senjen, R Proceedings of the Dioxin 2012 Conference, Cairns, Australia.

[11] www.industry.qld.gov.au/documents/LNG/csg-water-beneficial-use-approval.pdf. Also see Stuart J. Khan Quantitative chemical exposure assessment for water recycling schemes, Waterlines Report Series No 27, March 2010 Commissioned by the National Water Commission. Chemicals unable to be treated successfully include bromoform, chloroform, naphthalene, nonylphenol, octylphenol, dichloroacetic acid, trichloroethylene.

[12] http://www.aquatechnology.net/reverse_osmosis.html

Benzene, Toluene, Ethylbenzene, Xylene or BTEX are natural volatile compounds (VOCs) released from the coal seam. Their short term health effects include skin, eye / nose irritation, dizziness, headache, loss of coordination and impacts to respiratory system. Chronic exposure can result in damage to kidneys, liver and blood system. Benzene is strongly linked with leukemia[13] and diseases such non hodgkins non-Hodgkin's lymphoma (NHL).

Other Volatile Organic compounds can also be toxic. Some are known to cause cancer in animals (eg methylene chloride), or in humans (eg formaldehyde) or are suspected human carcinogens (eg chloroform and bromodichloromethane). VOCs are also key ingredients in forming ozone (smog), which is linked to asthma attacks, and other serious health effects. VOCs help form fine particle pollution (PM2.5). VOC exposure may result in eye, nose, and throat irritation; headaches, visual disorders, memory impairment, loss of coordination, nausea, damage to liver, kidney, and central nervous system.[14]

Contamination risks to ground and surface water include leakage of drilling fluids from the well bore into near surface aquifers; poor cement jobs on well bore casing, fracking pressure resulting in cracks in the well casing allowing leakage of fluids; contamination from flow back fluid; accidental spills of fluids or solids at the surface; surface and subsurface blow outs; chemicals remaining in the underground from repeated fracking or naturally occurring contaminants finding their way from the producing zone to shallow or drinking water aquifers through fractures in the rock; and/or discharge of insufficiently treated waste water into surface water or underground.[15]

US EPA investigation of water contamination in 23 drinking water wells near a natural gas extraction site in Wyoming concluded that both *inorganic and organic compounds associated with hydraulic fracturing have contaminated the aquifer at or below the depths used for domestic water supply in the Pavillion area.*[16] In Australia, BTEX chemicals have been found in monitoring wells associated with CSG activities; for example, in five of 14 bores at Arrow Energy's gas fields, near Dalby. Benzene was detected at levels between 6 to 15 times the Australian drinking water standard (0.001 milligram per litre /1ppb).[17] Toluene and methane have been detected in a private drinking water bore in Queensland. [18]

Methane Water Contamination

An analysis of 60 water wells near active gas wells in the US[19] found most were contaminated with methane at levels well above US federal safety guidelines for methane. The majority of water wells situated one kilometre or less from a gas well, contained water contaminated with 19 to 64 parts per million of methane. Wells more than a kilometre from active gas had only a few parts per million of methane in their water. The study used chemical and isotopic analyses to identify the high levels of methane in well water as being produced in the deep shale, released by gas drilling activities. Sampling of CSG released water from Bohena Creek in the Pilliga Forest NSW detected methane at the Eastern Star Gas discharge site at 68 micrograms per litre (ug/l), whereas it was not detected in the upstream control sample.[20]

Drilling muds, which are produced in large quantities due to well numbers, include toxic drilling additives, salt compounds, heavy metals, NORMs and hydrocarbons.[21] They are often disposed of in landfill and more recently, in land-spraying on agricultural or rural lands.

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[13] Rinsky, R.A Benzene and leukemia: an epidemiologic risk assessment. *Environ Health Perspect*. 1989 July; 82: 189–191.

[14] http://www.epa.gov/iaq/voc.html

[15] Potential Risks for the Environment and Human Health Arising from Hydrocarbons Operations Involving Hydraulic Fracturing in Europe. http://ec.europa.eu/environment/integration/energy/pdf/fracking%20study.pdf

[16] http://www.epa.gov/region8/superfund/wy/pavillion/EPA_ReportOnPavillion_Dec-8-2011.pdf

[17] Media Release 'Arrow advises of monitoring results' 26 August 2011

[18] Simtars Investigation of Kogn Water Bore (RN147705) -16 October 2012

[19] Osborn, SG, A Vengosh, NR Warner, RB Jackson. 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. Proceedings of the National Academy of Sciences, U.S.A. doi: 10.1073/pnas.1100682108. http://www.nicholas.duke.edu/cgc/pnas2011.pdf

[20] Water sampling results supplied by East West Enviroag as Project No. EW 110647.

[21] Origin's Environmental Management Plan Landspraying While Drilling (LWD) Trial Program OEUP-Q8200-PLN-ENV-002

Radioactive Materials, Naturally Occurring Radioactive Materials (NORMs) are found in coal seams and shale, eg uranium, thorium, radium-228 and radium-226.[22] The radioactive material can be released through the drilling process in drill cuttings/muds and flowback water. Radium is a known carcinogen[23] and exposure can result in increased incidence of bone, liver and breast cancer. Radon, a decay product of radium can cause lung cancer.

Air pollution has been demonstrated in a 2012 study,[24] where 44 hazardous air pollutants were detected at gas drilling sites. The 12 month study found a wide range of air toxics including methane, methylene chloride, ethane, methanol, ethanol, acetone, and propane, formaldehyde, acetaldehyde, PAHs / naphthalene. They noted a great deal of variability across sampling dates in the numbers and concentrations of chemicals detected. Notably, the highest percentage of detections occurred during the initial drilling phase, prior to hydraulic fracturing on the well pad. Air toxics can cause cancer and other serious, irreversible health effects, such as neurological problems and birth defects.[25]

Flaring (the burning off of natural gas from a new well) releases hydrogen sulfide, methane and BTEX chemicals (benzene, toluene, ethylbenzene, and xylene) into the air,[26] as well as metals such as mercury, arsenic and chromium. The US EPA has banned flaring after January 2015. [27]

Gas Processing is required to remove impurities before natural gas can be used as a fuel. The by-products include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, hydrogen sulphide, carbon dioxide, water vapor and sometimes helium and nitrogen.

Human exposure can occur through direct skin contact with the chemicals or wastes; drinking or bathing in contaminated water; by breathing in vapors from flowback, evaporation ponds or stored wastes; and through contaminated dust particulates. There are many incidents of communities reporting adverse human and animal health impacts.

A Human Health Risk Assessment of air emissions around US UG activities,[28] concluded that residents closest to well pads i.e., living less that 1/2 mile from wells, have higher risks for respiratory and neurological effects based on their exposure to air pollutants; and a higher excess lifetime risk for cancer. The study took 163 measurements from fixed monitoring station, 24 samples from perimeter of well pads (130-500 feet from center) undergoing well completion and measured ambient air hydrocarbon emissions. Emissions measured by the fenceline at well completion were statistically higher ($p \leq 0.05$) than emissions at the fixed location station (inc. benzene, toluene, and several alkanes.) The assessment was based on the US EPA guidance to estimate non-cancer and cancer risks for residents living greater 1/2 mile from wells and residents living equal to or less than a 1/2 mile from wells. The study may have underestimated risks to human health as it did not measure ozone or particulates. USEPA methods may also underestimate health risks of mixed exposures.

US Health Survey [29] investigated the extent and types of health symptoms experienced by people living near UG in Pennsylvania. Environmental testing was conducted on the properties of a subset of survey participants (70 people in total) to identify the presence of pollutants that might be linked to both gas development and health symptoms. Test locations

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[22] Fact Sheet FS-163-97 October, 1997 Radioactive Elements in Coal and Fly Ash: Abundance, Forms, and Environmental Significance, USGShttp://pubs.usgs.gov/fs/1997/fs163-97/FS-163-97.html
[23] http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=790&tid=154
[24] Colborn T, Schultz K, Herrick L, and Kwiatkowski C. 2012 (in press). An exploratory study of air quality near natural gas operations. *Hum Ecol Risk Assess*
[25] http://www.epa.gov/airquality/oilandgas/pdfs/20120417presentation.pdf
[26] http://www.hsph.harvard.edu/research/niehs/files/penning_marcellusshale.pdf
[27] http://www.epa.gov/airquality/oilandgas/pdfs/20120417presentation.pdf
[28] Lisa M. Mckenzie, Roxana Z. Witter, Lee S. Newman and John L. Adgate, Human health risk assessment of air emissions from development of unconventional natural gas resources." *Science of the Total Environment* March 21, 2012
[29] Gas Patch Roulette: How Shale Gas Development Risks Public Health In Pennsylvania, October 2012 Earthworks' Oil & Gas Accountability Project • www.earthworksaction.org

were selected based on household interest, the severity of symptoms reported, and proximity to gas facilities and activities. In total, 34 air tests and 9 water tests were conducted at 35 households in 9 counties. VOCs were detected in air including 2-Butanone Acetone, Chloromethane, Carbon tetrachloride, Trichlorofluoromethane, Toluene, Methylene Chloride, Dichlorodifluoromethane, n-Hexane, Benzene, Tetrachloroethylene , 1,2,4-Trimethylbenzene, Ethylbenzene, Trichloroethylene, Xylene and 1,2-Dichloroethane**.** A range of symptoms were reported in the 108 surveys including nasal & throat irritation (60%), sinus problems (58%), eyes burning (53%), shortness of breath (52%), difficulty breathing (41%), severe headaches (51%), sleep disturbance (51%), frequent nausea (39%), skin irritation (38%), skin rashes (37%), dizziness (34%). While the study did not prove that living closer to an oil and gas facility causes health problems, they did suggest a strong association, as in general, the closer to gas facilities respondents lived, the higher the rates of symptoms they reported.

Residents of Tara Queensland have reported similar symptoms including severe headaches, nausea, vomiting, nose bleeds, rashes, eye and throat irritations and severe skin irritations. Single grab samples of ambient air taken in communities around UG activities have detected VOCs, including ethanol, acetone, benzene, toluene, xylene, ethylbenzene, dichlorodifluoromethane, 1,2,4-trimethylbenzene, naphthalene, phenylmaleic anhydride, methyl ethyl ketone, phenol, butane, pentane, hexane.

Annex 1

Hydraulic fracturing fluids usually include:

- **Gelling agents** to hold the proppant in suspension (eg mixtures of industrial guar gum, diesel, alkanes/alkenes);
- **Gel stabilisers** (eg sodium thiosulphate) and **gel breakers** (eg Ammonium persulfate, sodium persulfate);
- **Friction reducers** to ease pumping and evacuation of fluid (eg polyacrylamide, mixtures of methanol, ethylene glycol, surfactants /fluorocarbon surfactants);
- **Diluted acid** to dissolve minerals (eg hydrochloric acid, muriatic acid);
- **Biocides** to prevent bacterial action underground (eg glutaraldehyde, Tetrakis
- hydoxymethyl phosphonium sulfate / THPS, 2-Bromo-2-nitro-1,3-propanediol (Bronopol), 2,2-Dibromo-3-nitrilopropionamide (DBNPA);
- **Clay stabilisers** to prevent clay expanding on contact with water and plugging the reservoir (eg tetramethyl ammonium chloride); and
- **Buffer fluids** and **crosslinking agents**.

Fracking may also use:

- **Corrosion inhibitors (**eg formamide, methanol, naphthalene, naptha, nonyl phenols, acetaldhyde);
- **Scale inhibitors** (eg ethylene glycols);
- I**ron control** (eg citric acid, thioglycolic acid);
- **pH adjusting agents** (sodium or potassium carbonate); and
- **various surfactants** to affect fluid viscosity (eg isopropanol, 2-Butoxyethanol /2-BE.)

Drilling fluid components include:

- **Viscosifiers** to increase viscosity of mud to suspend cuttings (eg bentonite, polyacrylamide)
- **Weighting agent** (eg barium sulphate)
- **Bactericides/biocides** to prevent biodegradation of organic additives (eg glutaraldehyde)
- **Corrosion inhibitors** to prevent corrosion of drill string by acids and acid gases (eg zinc carbonate, sodium polyacrylate, ammonium bisulphate)
- **Defoamers** to reduce mud foaming (eg glycol blends, light aromatic and aliphatic oil, naptha)
- **Emulsifiers and deemulsifiers** to help the formation of stable dispersion of insoluble liquids in water phase of mud.
- **Lubricants** to reduce torque and drag on the drill string (eg chlorinated paraffins)
- **Shale control inhibitors** to control hydration of shales that causes swelling and dispersion of shale, collapsing the wellbore wall (eg anionic polyacrylamide, acrylamide copolymer, petroleum distillates)

- **Polymer stabilisers** to prevent degradation of polymers to maintain fluid properties (eg Sodium sulfite).
- **Breakers** to reduce the viscosity of the drilling mud by breaking down long chain emulsifier molecules into shorter molecules
- **Salts** (eg potassium chloride, sodium chloride, calcium chloride)

The Persistent Organic Pollutant, perfluorooctane sulfonate (PFOS) is permitted in hydraulic fracturing fluids under an exemption to the *Stockholm Convention on POPs* 2001.[30] Chlorinated paraffins are also used in drilling fluids, with POPs chemicals, short chain chlorinated paraffins (SCCPs) listed in drilling fluid patents. POPs are recognised as the most dangerous of all man made chemicals.

Annex 2
Examples of UG Chemicals and their Environmental Health Effects

Ethylene Glycol, a known human respiratory toxicant and associated with increased risks of spontaneous abortion and sub-fertility in female workers;

2-Butoxyethanol, a highly mobile and persistent contaminant of groundwater, which can cause reproductive problems and birth defects in animals, and destruction of red blood cells;

Ethoxylated 4-nonylphenol, a persistent, bioaccumulative, endocrine disruptor, very toxic to aquatic organisms and causing sexual deformities in exposed oyster larvae, found to increase the incidence of breast cancer in lab animals;

Methanol, a volatile organic compound, highly toxic to humans (most commonly used chemical)[31];

Isopropanol, central nervous system depressant capable of causing degenerative changes in the brains of lab animals;

Formamide, a teratogen with the potential to affect the unborn child, which can be absorbed into the body by inhalation and through the skin;

Naphthalene, causes nasal and lung tumours and is listed by International Agency for Research into Cancer (IARC) as *possible human carcinogen'.* The US Department of Health and Humans Service found it to be *'reasonably anticipated to be a human carcinogen'.*

Chemicals used by the Australian UG industry have found to be 'dangerous at concentrations near or below chemical detection limits by the State University of New York. [32] These include glutaraldehyde, brominated biocides (DBNPA, DBAN), propargyl alcohol, 2-butoxyethanol (2-BE) and heavy naphtha.

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[30] http://www.pops.int
[31] Methanol was used in 342 of the 750 hydraulic fracturing products used in the US. It is a hazardous air pollutant and on the candidate list for potential regulation under the US *Safe Drinking Water Act* due to its risks to human health. See United States House of Representatives Committee on Energy and Commerce, Minority Staff, April 2011 Chemicals Used In Hydraulic Fracturing. http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf
[32] Chemical and Biological Risk Assessment for Natural Gas Extraction in New York. Ronald E. Bishop, Ph.D., CHO, Chemistry & Biochemistry Department, State University of New York, College at Oneonta, Sustainable Otsego March 28, 2011. www.sustainableotsego.org/Risk%20Assessment%20Natural%20Gas%20Extraction-1.htm