Toxic Chemicals in the Exploration and Production of Gas from Unconventional Sources

Queensland Gas Fields

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> *'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, methane hydrates and underground coal gasification. Natural gas consists primarily of methane with other hydrocarbons, carbon dioxide, nitrogen and hydrogen sulfide.

Shale gas is found in the fractures and pore spaces of natural shale. 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. [3]

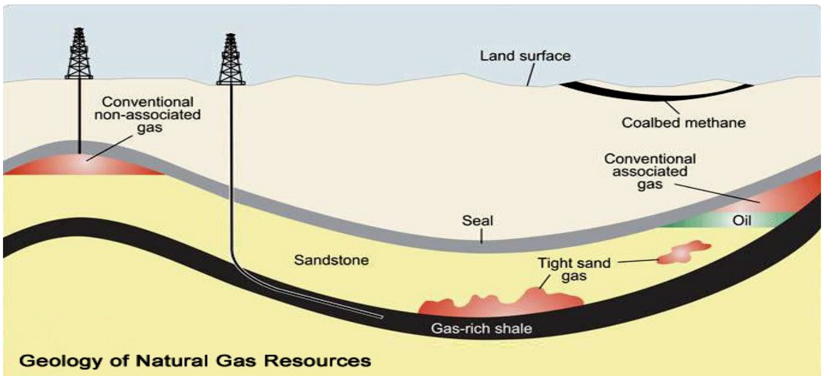
Tight gas is trapped in hard impermeable rock underground (eg sandstone, limestone). Tight gas wells need to be fracked to achieve gas flow. This is often followed by acidation, which involves pumping acids into the well to dissolve the limestone and the calcite cement between the sediment grains of the reservoir rocks. This process re-establishes the natural fissures that were present in the formation before compaction and cementation occurred.

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. [4]

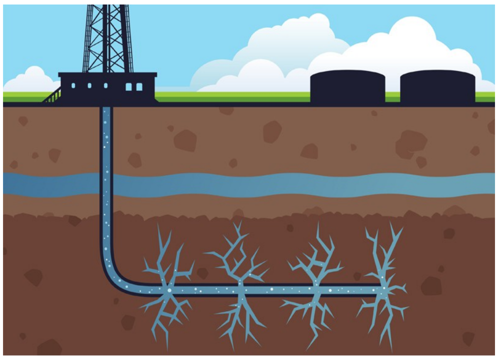
A significant difference between shale gas and CSG is the depth at which they are found. Shale gas reservoirs are typically found at 2,000 to 2,300 metres below ground, deeper than coal bed methane reservoirs, which are situated at 800 to 1,200 metres. The closer the gas reservoirs are to ground water aquifers the greater the chance of hydraulic communication with that aquifer.

Lifespan of a well is 5 to 15 years with output typically declining by between 50% and 75% in the first year of production. Most recoverable gas is usually extracted after just a few years.[5]

Underground coal gasification (UCG) is the process where coal is converted to gas underground via forced combustion. Three pilot projects were initiated in Australia with two being closed due to pollution issues and concerns over unacceptable risks of environmental harm.[6]



Hydraulic fracturing *(fracking/HF)* involves injecting wells at high pressure with water, proppants, radioactive tracers and chemical additives to fracture the formation and produce new cracks and pathways to help extract the gas. While chemical additives make up less than 2% of the fracking fluid, this still translates to large quantities. An estimated 18,500 kilograms were used in a CSG fracking in Australia with up to 40% not recovered.[7] The European Parliamentreport estimates 16 tonnes of acute toxic substances was used to frack tight gas in Lower Saxony, Germany.[8] A well may be 'fracked' a number of times.


Hydraulic Fracturing Diagram

Over 750 chemical products with 650 containing hazardous substances and 279 products with trade secrets were identified by the US House of Representatives Committee on Energy and Commerce.[9] These include carcinogens (eg naphthalene), neurotoxins (eg isopropanol*),* irritants/sensitisers (eg sodium persulfate*)*, reproductive toxins (eg ethylene glycol) and endocrine disruptors [10] (eg nonylphenol). Some of the chemicals have been found to be dangerous at concentrations near or below chemical detection limits,[11] (eg glutaraldehyde, brominated biocides (DBNPA, DBAN), propargyl alcohol, 2-butoxyethanol (2-BE), heavy naphtha.)

Many chemicals have not been assessed for their long-term impacts on the environment and human health. In Australia, 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 for their use in CSG.[12] The mixtures used in drilling and fracking fluids are also not assessed for toxicity or persistence and can form new compounds when exposed to sunlight, water, air, radioactive elements or other natural chemical catalysts.

Industry self-reporting on 9,310 individual US fracking operations between January 2011 and September 2012, noted cancer causing chemicals were used in one out of every three HF 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 HF operations.[13]

Sand, proppants and particulates are an integral part of UG activities. The formation and distribution of particulate pollution comes from a range of sources including transport, diesel engines and the use of proppants in HF. Up to 50,000 kg of proppants was reported as being used in the HF of shale in Western Australia.[14] Proppants consist of either sand/silica or manufactured ceramic polymer spheres based on alumino-silicates, which are injected as part of the fracturing fluid mixture and intended to 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.[15] The US National Institute for Occupational Safety and Health (NIOSH) have released a Hazard Alert, identifying exposure to airborne silica as a health hazard to workers conducting HF operations.[16] According to a Haliburton patent[17] acrylic polymers consisting of 85% acrylonitrile (human carcinogen) are used for proppant spheres. Acrylonitrile has been detected in US air sampling of gas sites at high levels.[18]

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, (benzene, toluene, ethylbenzene, xylene), polycyclic aromatic hydrocarbons (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', detected VOCs (bromodichloromethane, bromoform, chloroform and dibromochloromethane), as well as benzene and chromium, copper, nickel, zinc.[19]

Produced Waste Water used for Dust Suppression

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).[20] The amount of produced water from a CSG well varies between 0.1 - 0.8 megalitres (ML) per day.[21] 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. Low molecular weight, non polar, water-soluble solutes such as the methanol and ethylene glycol are poorly rejected.[22]

Benzene, Toluene, Ethylbenzene, Xylene or BTEX are volatile organic compounds (VOCs) found naturally in crude oil, coal and gas deposits and associated groundwater.[23] These can be released from the coal seam via drill holes or fractures.[24] The short term health effects of BTEX 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[25] and diseases such non hodgkins non-Hodgkin's lymphoma (NHL).

Other VOCs 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, 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.[26]

Naturally occurring radioactive materials (NORMs) are found in coal seams and shale, eg uranium, thorium, radium-228 and radium-226.[27] The radioactive material can be released through the drilling process in drill cuttings/muds and flowback water. Radium is a known carcinogen and exposure can result in increased incidence of bone, liver and breast cancer. Radon, a decay product of radium can cause lung cancer. The level of reported radioactivity varies significantly, depending on the radioactivity of the reservoir rock and the salinity of the water co-produced from the well. The higher the salinity the more NORM is likely to be mobilized. Since salinity often increase with the age of a well, old wells tend to exhibit higher NORM levels than younger ones.[28]

Drilling muds, which are produced in large quantities due to well numbers, include toxic drilling additives, salt compounds, heavy metals, NORMs and hydrocarbons.[29] They are often disposed of in landfill and more recently, in land-spraying on agricultural or rural lands.

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 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 aquifers.[30]

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.*[31] A number of synthetic organic compounds were detected including BTEX and isopropanol (biocide, surfactant, used in breakers, in foaming agents), diethylene glycol (foaming agent), triethylene glycol (solvent), tert-butyl alcohol (known breakdown product of methyl tert-butyl ether (fuel additive) and tert-butyl hydroperoxide (gel breaker used in hydraulic fracturing) plus diesel and gasoline organics. The detections of organic chemicals were more numerous and at higher concentrations in the deeper of the monitoring wells. Detection of high concentrations of benzene, xylenes, gasoline range organics, diesel range organics, and total purgeable hydrocarbons in ground water samples from shallow monitoring wells near pits indicated that they a source of shallow ground water contamination. The report also found that elevated levels of dissolved methane in domestic wells generally increase in those wells in closer proximity to gas production wells.

In Australia, BTEX chemicals have been found in 5 out of 14 monitoring wells at Arrow Energy's gas fields, near Dalby, Queensland. Benzene was detected at levels 6 and 15 times the Australian drinking water standard (0.001 milligram per litre /1ppb).[32] Toluene and methane have been detected in a private drinking water bore in Queensland.[33]

Methane contamination of water was evident in an analysis of 60 water wells near active gas wells in the US.[34] Most were contaminated with methane at levels well above US federal government 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. In Australia, sampling of CSG released water from Bohena Creek in the Pilliga Forest, New South Wales, 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.[35]

Air pollution has been demonstrated in a 2012 study,[36] 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.[37]

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,[38] as well as metals such as mercury, arsenic and chromium.

The US EPA has banned flaring after January 2015.[39]

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.

Australia Research on fugitive emissions [40] used atmospheric radon (^{222}Rn) and carbon dioxide (CO2) concentrations to measure fugitive emissions in the CSG fields of the Tara region, Queensland. They measured a 3 fold increase in maximum ^{222}Rn concentration inside the gas field compared to outside and also a significant relationship with the number of wells. They suggest that CSG activities may change the geological structure and enhance diffuse soil gas exchange processes, helping gases to seep through the soil to be released to the atmosphere. The presence of ^{222}Rn and CO2 suggests the release of other gaseous substances, such as VOCs, which can be very harmful to human health.

Human exposure can occur through direct skin contact with the chemicals or wastes; drinking or bathing in contaminated water (surface, bore/well); 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[41] 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 than 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 [42] 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 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 and 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, it did suggest a strong association, as in general, the closer to gas facilities respondents lived, the higher the rates of symptoms they reported.

Foam spewing from a CSG well in outer Sydney Australia.

Residents of Tara Queensland have reported similar symptoms including severe headaches, nausea, vomiting, nose bleeds, rashes, eye and throat irritations and severe skin irritations. Limited sampling of ambient air undertaken around the Tara estate near CSG 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. Toluene, a neurotoxin was found in the air around a number of Tara homes and in the air above a resident's water bore. In the latter [33] the level (0.33ppm) was dismissed as below levels of concern, yet was well above the 'Chronic Reference Exposure Limits' used for long-term exposure by California, Massachusetts, Michigan states in the USA.

Queensland Department of Health Report 'Coal seam gas in the Tara region: Summary risk assessment of health complaints and environmental monitoring data', March 2013 was unable to determine whether any of the health effects reported by the community are linked to exposure to CSG activities, but *'did provide some evidence that might associate some of the residents' symptoms to exposures to airborne contaminants arising from CSG activities.'* The industry's sampling on which the report relies was very limited in both scope and time, yet still detected a wide range of VOCs in the air around homes in Tara. For many of the chemicals, the level of detection used by the laboratories was above the level set for the protection of health. Benzene, a confirmed human carcinogen, was detected at levels above the health criteria, yet the results were dismissed with the claim that 'benzene was not a compound that is found in CSG and therefore cannot be attributed to CSG activities'. This is despite the Queensland's Department of Environment and Heritage Protection website stating that BTEX compounds like benzene, toluene, ethylbenzene, xylene are found naturally in gas deposits and therefore they can be naturally present at low concentrations in groundwater near these deposits.[23]

The Health Report acknowledged that industry air monitoring on which it was based had important limitations. The total monitoring period was only nine days, the methodology resulted in limits of reporting for some chemicals that were substantially higher than the reference air quality criteria and that the monitoring was not designed to identify short-term peaks or troughs in air concentrations. The Health Study did not include an assessment of aggregate exposure, of particular concern for the children of Tara. Of the 11 families and 56 people reporting symptoms (headache, rashes, sore eyes, nausea, nosebleeds), only 15 were seen in person by the government appointed doctor.

Methane Leaks Bubbling in the Condamine River Queensland

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);
- **Surfactants** to affect fluid viscosity (eg isopropanol, 2-Butoxyethanol /2-BE)
- **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**.

  They may also use:
- **Corrosion inhibitors (**eg formamide, methanol, naphthalene, naptha, nonyl phenols, acetaldhyde);
- **Scale inhibitors** (eg ethylene glycols);
- **Iron control** (eg citric acid, thioglycolic acid);
- **pH adjusting agents** (sodium or potassium carbonate); and
- **Diluted acid** to dissolve minerals (eg hydrochloric acid, muriatic acid);

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 (eg diammonium peroxydisulphate, hemicellulase enzyme)

- **Salts** (eg potassium chloride, sodium chloride, calcium chloride)

Persistent Organic Pollutant (POPs): perfluorooctane sulfonic acid (PFOS) is permitted in hydraulic fracturing fluids under an exemption to the *Stockholm Convention on POPs* 2001.[43] Chlorinated paraffins are used in drilling fluids, with the 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

Note: The following information was compiled from publically available sources including International Program on Chemical Safety, INCHEM, www.inchem.org, US Agency for Toxic Substances & Disease Register, www.atsdr.cdc.gov, Material Safety Data Sheets and NICNAS literature.
Health data and sources for 560 fracking chemicals is available for download at http://www.endocrinedisruption.com/chemicals.multistate.php

2-Butoxyethanol
2-butoxyethanol was declared a Priority Existing Chemical under NICNAS.[44] The assessment of 2-butoxyethanol shows that it is highly mobile in soil and water and has been detected in aquifers underlying municipal landfills and hazardous waste sites in the US. It is recommended that waste 2-butoxyethanol not be disposed of to landfill because of its high mobility, low degradation and its demonstrated ability to leach into and contaminate groundwater. High doses of 2-butoxyethanol can cause reproductive problems and birth defects in animals. Animal studies have shown exposure to 2-butoxyethanol can cause hemolysis (destruction of red blood cells that results in the release of hemoglobin). The International Agency for Research on Cancer has not classified 2-butoxyethanol as to its human carcinogenicity as no carcinogenicity studies are available.

Ethoxylated 4-nonylphenol
Ethoxylated 4-nonylphenol (NPE) is a persistent bioaccumulative endocrine disrupting chemical (EDC), which has been detected widely in wastewater and surface waters across the globe. NPE disrupt normal hormonal functioning in the body. It can mimic the natural hormone estradiol and binds to the estrogen receptor in living organisms. Exposure to NPE changes the reproductive organs of aquatic organisms.[45] Sexual deformities were found in oyster larvae exposed to levels of nonylphenol (NP) that are often present in the aquatic environment.[46] A 2005 study found that exposure to NP increases the incidence of breast cancer in lab mice.[47] Canada classified NPE metabolites as toxic.[48] The European Union classifies nonylphenol as very toxic to aquatic organisms, which may cause long-term adverse effects in the aquatic environment.[49] The intermediary chemicals formed from the initial degradation of NPE are much more persistent than the original compound.

Ethylene Glycol
Exposure to ethylene glycol via inhalation or skin contact can irritate the eyes, nose and throat. It is a human respiratory toxicant. Among female workers, exposures to mixtures containing ethylene glycol were associated with increased risks of spontaneous abortion and sub-fertility.[50] Ethylene glycol is a teratogen (i.e., an agent that causes malformation of an embryo or foetus) in animal tests. Ethylene Glycol is on the U.S. EPA list of 134 priority chemicals to be screened as an endocrine disrupting substance (EDC).

Formamide
Formamide is a teratogen with the potential to affect the unborn child. It is irritating to the eyes and the skin and may cause effects on the central nervous system. It can be absorbed into the body by inhalation, through the skin and by ingestion.

Glutaraldehyde
Glutaraldehyde is highly irritating to the eyes, skin [51] and the respiratory tract of humans and laboratory animals. It has induced skin sensitization in humans and laboratory animals, and caused asthma in occupationally exposed people.[52] In animal tests, glutaraldehyde by inhalation caused lung damage in rats and mice. DNA damage, mutations and some evidence of chromosome damage were found in mammalian cells in culture following treatment with glutaraldehyde. Data indicates that both algae and fish embryos may be particularly sensitive to long-term glutaraldehyde exposure.[53]

Isopropanol
Isopropanol is reproductive toxin and irritant. It is a central nervous system depressant and prolonged inhalation exposure of rats can produce degenerative changes in the brain.[54]

Methanol
Methanol is a volatile organic compound, which is highly toxic to humans. Methanol causes central nervous system depression in humans and animals as well as degenerative changes in the brain and visual system. Chronic exposure to methanol, either orally or by inhalation, causes headache, insomnia, gastrointestinal problems, and blindness in humans and hepatic and brain alterations in animals. Methanol is highly mobile in soil. In water, the degradation products of methanol are methane and carbon dioxide. Methanol also volatilizes from water and once in air, exists in the vapor phase with a half-life of over 2 weeks. The chemical reacts with photochemically produced smog to produce formaldehyde and can also react with nitrogen dioxide in polluted air to form methyl nitrite.[55] Methanol is listed as the most commonly used HF chemical by the United States House of Representatives Committee on Energy and Commerce.[56]

Naphthalene
Chronic exposure of workers and rodents to naphthalene has been reported to cause cataracts and damage to the retina. Based on the results from animal studies, which demonstrated nasal and lung tumours in lab animals, US EPA and the International Agency for Research on Cancer (IARC) has classified naphthalene as a Group C, possible human carcinogen.[57] Animal studies suggest that naphthalene is readily absorbed following oral or inhalation exposure. Although no data are available from human studies on absorption of naphthalene, the detection of metabolites in the urine of workers indicates that absorption does occur, and there is a good correlation between exposure to naphthalene and the amount of 1-naphthol excreted in the urine.

Sodium Persulfate
Exposure to sodium persulfate via inhalation or skin contact can cause sensitization, i.e., after initial exposures individuals may subsequently react to exposure at very low levels of that substance. Exposure can also cause skin rashes and eczema. Sodium persulfate is irritating to eyes and respiratory system and long-term exposure may cause changes in lung function (i.e. pneumoconiosis resulting in disease of the airways) and/or asthma.

Tetrakis (hydroxymethyl)phosphonium sulfate (THPS)
THPS is toxic to microorganisms Repeated skin exposure to THPS resulted in severe skin reaction and caused skin sensitization in guinea pigs. THPS was also identified as a severe eye irritant in rabbits.[58] It has shown mutagenic potential (in vitro) and cancer potential in rats. The reported acute toxicity values for algae are less than 1 milligram per litre (No Observable Effect Concentration (NOEC) of 0.06mg/litre). No exposure information is available for either humans or organisms in the environment; hence no quantitative risk assessment has been made.[59] Little is known about the effects of the break down products of THPS.

Holding Pond

Large Holding Pond

END NOTES

[1.] This brief is 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, NTN / IPEN
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National Toxics Network

The National Toxics Network Inc. (NTN) was formed in 1993 and has charity status.
It is a community-based network of experts and campaigners working on a wide range of toxic chemical and pollution issues across Australasian region including New Zealand, the Pacific and South East Asia. NTN is the Australian focal point for IPEN, the International Persistent Organic Pollutants Elimination Network (IPEN) and also participates in the work of the international Pesticide Action Network (PAN) and the Global AlliaNce for Incineration Alternatives (GAIA). In Australia, NTN is a supporting member of the Australian Environment Network (AEN), Climate Action Network Australia (CANA) and the Lock the Gate Alliance.

For further details about the National Toxics Network please visit www.ntn.org.au
and www.facebook.com/ntn

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