HALOGENATED CONTAMINANTS FROM COAL SEAM GAS ACTIVITIES

Lloyd-Smith M[1]*, Senjen R[2]

[1]National Toxics Network/ IPEN, Bangalow Australia; [2]Monash University, School of Political & Social Inquiry, Melbourne Australia

Introduction

Coal Seam Gas (CSG) activities are rapidly expanding in Australia with a predicted 40,000 wells, to be developed in the state of Queensland alone. Community concern over the contamination of groundwater, surface waste and air is growing, with much of the farming community and environmentalists opposing further development of CSG gas fields. There is limited publicly available data on chemical use and release, and little is known about the formation and release of halogenated compounds associated with CSG activities. As many halogenated compounds have been found to be toxic, persistent and capable of transboundary movement,[1] this study focused on their use and release by the CSG industry in Australia and aims to highlight the need for governments to provide comprehensive hazard assessment for all chemicals used, generated and released in Australian CSG activities.

Materials and methods

The study was based on a participatory research model, which brings together researchers and community members, in order to identify problems and foster a shared understanding of the issues facing the community.[2] It aims to empower community members to better understand the problems they face, to create solutions to these problems, and to improve conditions in the community.

In late 2010, the National Toxic Network (NTN) was provided with a range of environmental impact assessments and commercial risk assessments that had been submitted by CSG companies to government agencies in support of their CSG projects. NTN reviewed these, as well as other regulatory permits and scientific reports, and consolidated the available data on chemical use and releases of CSG activities in Australia.[3] In cooperation with local communities, NTN then undertook limited opportunistic environmental sampling. Three air samples using 8 hour canisters were taken from around CSG activities and a range of water samples were collected by community members. All were analysed by NATA accredited laboratories.

Results and discussion

From the review of industry documents, it was apparent that in some cases large quantities of chemical additives are used both at the drilling stage and during hydraulic fracturing, *('fracking')*. A risk assessment provided to the Queensland Department of Environment and Resource Management (DERM) identified approximately 18,500 kilograms of chemical additive used per well with up to 40% (7,500 kg) not recovered.[4] The chemicals used consisted of surfactants, lubricants, acids, scale/corrosion inhibitors and biocides. The identity of some chemicals could not be established from their Material Safety Data Sheet (MSDS) and of those identified, many had acute or chronic toxicity warnings on the MSDS or had adverse findings reported in the scientific literature. The majority of the chemicals had only limited data on environmental fate and ecotoxicology. Of the 23 identified as commonly used fracking chemicals in Australia, only two (2-Butoxyethanol, Sodium Persulfate) had been assessed by the national industrial chemical regulator, National Industrial Chemicals Notification and Assessment Scheme (NICNAS) and neither assessment was for their use in CSG. The list of 23 also included halogenated substances such as the brominated biocides.

The Australian Petroleum Production and Exploration Association (APPEA) provides a list of approximately 46 substances used in production and exploration activities, but environmental impact assessments identified chemicals that were not on the APPEA list,[5] including 2-Bromo-2-nitro-1,3-propanediol (Bronopol) and 2,2-Dibromo-3-nitrilopropionamide (DBNPA). These are used as biocides in exploratory drilling, hydraulic fracturing and water treatment. DBNPA was among the chemicals identified as being dangerous at concentrations near or below their chemical detection limits.[6]

Waste Water Releases

CSG activities produce large quantities of *'produced'* water, the amount of which depends on the type and depth of the coal seam, but is reported by industry to range from 0.1 - 0.8 megalitres per day.[7] Produced water may be contaminated with heavy metals (e.g. cadmium, barium), naturally occurring radioactive substances (eg uranium, thorium) fracking or drilling chemicals, high concentrations and/or quantities of salt, [8] BTEX (benzene, toluene, ethylbenzene, xylene) and naturally formed halogenated chemicals. Halogenated compounds are listed in the permits for the release of *'produced water'*. Currently produced water in Australia is managed by disposal in evaporation ponds (covering many hectares), used for dust suppression on roads, or 'treated' and released into waterways, or sold on.

In Queensland, CSG projects permits to release produced water into the Murray Darling river system were provided for 18 months at a maximum volume of 20 megalitres per day. In one permit,[9] 80 chemical compounds as well as radionuclides were listed and included many halogenated substances.[10] Over an 18 month period, permitted releases into the Condamine River included over 20 tonnes of chlorobenzenes and approximately 32 tonnes of monochloramine and 76 tonnes of bromide. The release of bromide into waterways used for irrigation and drinking water supplies is of concern due to its potential to form brominated and mixed chloro-bromo byproducts such as trihalomethanes, or halogenated acetic acids. In 2011, dissolved bromine was detected in treated CSG water released at the NSW Pilliga Forest Eastern Star Gas discharge point in Bohena Creek at six times background levels (0.6 mg/L). [11] The use of reverse osmosis filtration to treat 'produced water' has limitations as it cannot remove all contaminants including bromoform, chloroform, dichloroacetic acid, trichloroethylene, tris(2-chloroethyl)-phosphate.[12]

Community Water Monitoring

Water samples were obtained by community members and were analysed for a range of contaminants including volatile and semivolatile compounds. A sample taken from the top of the well-head, a day after the well had been 'fracked', demonstrated the presence of bromodichloromethane (0.016 mg/L), bromoform (0.35 mg/L), chloroform (0.005 mg/L), dibromochloromethane (0.066 mg/L) as well as benzene (0.003 mg/l) and a range of metals (chromium, copper, nickel, zinc). Composite water samples also returned results which included phthalates, metals and halogenated compounds including Bis(2-chloroethoxy)methane (0.12 mg/L).[13]

The Australian New Zealand Environment and Conservation Council has not established trigger values for fresh and marine waters for the chlorinated alkanes due to insufficient data.[14] However, the US Hazardous Substances Data Bank (HSDB) [15] lists dibromochloromethane as moderately to highly mobile in soil and can leach into groundwater. It is reported to have an estimated half-life of 8.4 months in air, indicating that long-range global transport is possible. The International Agency for Research on Cancer has concluded that chloroform and bromodichloromethane are possibly carcinogenic to humans. Based on health considerations, the ANZECC Drinking Water guidelines state the concentration of chloroform, bromodichloromethane, dibromochloromethane, bromoform either individually or in total, in drinking water should not exceed 0.25 mg/L. In comparison, the USEPA has set Maximum Contaminant Level Goal (MCLG) for bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L): chloroform (0.07 mg/L).[16]

Community Air Monitoring

There is little air monitoring data in the public domain related to CSG activities in Australia. Farmers near Chinchilla in Queensland have reported noxious air emissions from a neighboring gas production, The company responded with offers of air conditioners and confidentiality agreements.[17] NTN in cooperation with local communities took three air samples from around gas extraction activities, including one taken adjacent to a residential water bore, using Low Level Air Canisters over an 8-hour period. The samples were analysed by the National Measurement Institute and were shown to contain ethanol and chlorofluorocarbons (CFCs).[18] Once used as refrigerants and aerosol spray propellant, because of their adverse impact on the ozone layer, CFCs were either banned or heavily regulated under the Montreal Protocol on Substances That Deplete the Ozone Layer, a protocol to the Vienna Convention for the Protection of the Ozone Layer). Dichlorodifluoromethane was detected in all samples at 0.46 - 2.8 ug/m3. Commonly known as R-12 or Freon-12, its manufacture was banned in the United States along with many other countries in 1994. Trichlorofluoromethane or Freon-11, which has the highest ozone depletion potential of any refrigerant, was detected in all samples at 0.24 - 1.6 ug/m3. Both these CFCs are recognised as halogenated substances that may be formed in natural processes, hence the source of these CFCs remains unknown. Whether they relate to old refrigerant equipment used by the CSG industry or naturally formed with their release facilitated by the processes of CSG requires further investigation. Community monitoring activities intend now to focus on chemical emissions from CSG flaring. Data on emissions from flaring is limited globally, [19] yet it is reported that over 250 pollutants have been identified as releases from oil and gas flaring. [20]

Findings Warrant Action

While these were very preliminary sampling results, they do indicate the need to assess the use and release of halogenated compounds in CSG activities. The research also highlights the need for CSG companies and State and Federal government agencies to provide comprehensive hazard assessment for all chemicals used in Australian CSG activities, including their impacts on human health, their ecotoxicology and environmental fate. As well, an environmental health assessment of all chemical releases associated with CSG activities including intentional venting, fugitive emissions, flaring, diesel use, waste water releases and treatment is long overdue. Currently with limited product information and inadequate data on releases, it is far from clear what halogenated substances are used in CSG activities or are released from wells and bores. With growing concern over the toxicity, persistence and long-range transport of halogenated substances, particular attention should be given to assessing their use and release.

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References:

1. Brown, T & Wania, F. (2008) *Environ. Sci. Technol*. 42*:* 5202–5209
2. Brown, L.D. & Tandon R. (1983) *Journal of Applied Behavioural Sciences*. 19(3): 277-294
3. National Toxic Network Report, Hydraulic Fracturing in Coal Seam Gas Mining: The Risks to our Health, Communities, Environment and Climate, 2011 Prepared by Lloyd-smith, M & Senjen, R http://www.ntn.org.au
4. 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
5. Australian Petroleum Production & Exploration Association Ltd (APPEA), Chemicals that may be used in Australian fracking fluid. http://www.appea.com.au
6. 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. http://www.sustainableotsego.org/Risk%20Assessment%20Natural%20Gas%20Extraction-1.htm
7. CSG and water: quenching the industry’s thirst, Gas Today Australia — May 2009
8. Arrow Energy: Salt Management; The amount of salt depends on the location and age of the coal seam, it is typically between five and eight tonnes (5000kg-8000kg) for every ML of water. Seawater has a salt concentration of 35,000ppm. http://www.arrowenergy.com.au/icms_docs/95251_Salt_Management.pdf
9. Schedule C, Australian Pacific LNG Pty Ltd Environmental Authority (petroleum activities) No. PEN100067807
10. These include: 1,1 Dichloroethene , 1,2 Dichlorobenzene, 1,2 Dichloroethane, 1,2 Dichloroethene, 1,4 Dichlorobenzene, 2,2 Dichloropropionic Acid, 2,4,5-Trichlorophenol, 2,4,6-Trichlorophenol, 2,4-Dichlorophenol, 2-Chlorophenol, 4-Chlorophenol, Bromochloroacetic acid, Bromochloracetonitrile, Bromochloromethane, Bromodichloromethane, Bromoform, Chloroacetic acid, Chlorobenzene, Chloroform, Dibromoacetic acid, Dibromoachloromethane, Dichloroacetic acid, Dichloroaceonitrile, Monochloramine Trichloroacetic acid.
11. Analytical Results ES1118565, 25-AUG-2011 East West Enviroag Project No. EW110647

12. Stuart J. Khan, (2010) Quantitative chemical exposure assessment for water recycling schemes, Waterlines Report, Series No 27, Commissioned by the National Water Commission.
13. Labmark Environmental Laboratories, Certificate of Analysis, Report 331850-W Composite: Roma Water Analysis, Mar 26, 2012
14. Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000 http://www.environment.gov.au/water/publications/quality/index.html
15. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
16. Drinking Water Contaminants http://water.epa.gov/drink/contaminants/index.cfm#7
17. Linc site causes big 'stink' 08 Aug, 2011 11:24 AM, Queensland Country Life
18. Australian Government National Measurement Institute, Report of Analysis of Air Canisters Low Level, Report No. RN900555 (2 Feb 2012), Report No. RN893233 (16 Dec 2011), Report No. RN893232 (16 Dec 2011)
19. Jiang M., Griffin W.M., Hendrickson C., Jaramillo P., Van Briesen J. & Venkatesh A. (2011) *Environ. Res. Lett.* 6(3): 034014
20. Canadian Public Health Association, Background to 2000; Resolution No.3 http://www.climatelaw.org/