Undetected Chemical Carcinogens released by Coal mining:
A new major health risk for Australia.

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Summary.
Coal consists of a complex mixture of organic chemicals, many having structures likely to cause mutations in DNA and the potential to cause cancer in humans. Polycyclic Aromatic Hydrocarbons, (PAHs) found in coal are amongst the most potent carcinogens known. A few of these chemicals have been studied and listed as possible carcinogens, but most, including those likely to be the most potent carcinogens, remain untested and therefore are largely not taken into account in assessing potential health risks.

Present legislated “safe” or maximum contamination levels are close to the level of detection for the few known carcinogens listed. Most potent carcinogens found in coal have not been studied or listed. They are likely to initiate cancer at concentrations that are orders of magnitude below their detectable levels in drinking water. So testing ground or drinking water may be of little use in determining cancer risk.

Testing of runn-off water is one possible way of detecting the carcinogens released from coal by the mining process. Testing air close to the minning operationl may detect particulate chemicals that can end up in run-off. However most routine air and water tests only list the top 5 or 10 Volatile Organic Compounds (VOC's) and leave out the chemicals of interest, with the exception of benzene. If PAH tests are carried out they may not be sensitive enoCMh to detect PAH's at levels that impose a cancer risk. Assays are often reported as negative, which is misleading as the chemicals of interest were not included in the assay results, and the chemical may still be present. More sensitive assays are needed for routine testing, and regular testing of produce water for PAHs should be manditory to assess the health risks of CM.

As many of the carcinogenic hydrocarbons and PAHs likely to be released by coal mininng (CM) are persistent, we need to legislate, and implement the recommendations below, to minimise the release of chemical carcinogens into the atmosphere and groundwater by CM. Air and water-borne carcinogens are increasing at alarming rates, along with esophageal cancer. By acting now, we can reduce the escalation of chemically induced cancer in future generations.

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Introduction.
This submission deals with the potent chemical carcinogens, mainly hydrocarbons, that are liberated from CM, and their effect on the health of people exposed to them. The main focus is on aromatic hydrocarbons, particularly PAHs and their derivatives, which are the most potent mutagens and thus the most likely of the chemicals released to increase cancer incidence. How they can best be monitored and cancer risks reduced is discussed in the light of what little information is available on them.

Chemical Carcinogens, Mutagens and Cancer.
The process of development of human tumors is complex,[1] but the underlying cause of the process is mutation of DNA. “Most evidence points to a multistep process of sequential alterations in several, often many, oncogenes, tumor-suppressor genes, or microRNA genes in cancer cells.”[2]

Carcinogens are classified according to their mode of action as genotoxic or nongenotoxic carcinogens. Genotoxic carcinogens initiate carcinogenesis by direct interaction with DNA, resulting in DNA damage or chromosomal aberrations that can be detected by genotoxicity tests eg. Ames Test[3]. Nongenotoxic carcinogens are agents that, at least initially, indirectly interact with DNA. These indirect modifications to DNA structure, amount, or function may result in altered gene expression or signal transduction[4].

A large range of chemical mutagens have been found to cause cancer in animal models.[5] Poly Aromatic Hydrocarbons (PAH) and their derivatives are among the most potent carcinogens, having structures that resemble the base pair in DNA and readily intercalating and/or covalently bonding to DNA causing mutation.[6,7] The effect of carcinogens in mixtures is complex and synergistic effects often occur.[8] Care must be taken in assessing risks from carcinogens from complex mixtures such as environmental samples.

Possible Coal Carcinogens
Coal consists of a complex mixture of organic chemicals, many having structures likely to cause mutations in DNA and the potential to cause cancer in humans. PAHs solubilised from coal samples ranged from 1.21 to 28.6 mg/kg, and this did not include compounds 4 rings or larger.[9] Amounts of US EPA specified PAHs extracted from coals in this study range from 0.28 to 6.38 mg/kg. Less than ¼ have been listed as possible carcinogens, the rest remain unstudied, and therefore are not classified by agencies like the International Agency for Research on Cancer(IARC), the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) or the National toxicology Program of the U.S.Department of Health and Human Services (NTP) as carcinogens or possible carcinogens. As they are not classified, the majority of carcinogens in coal and fracking chemicals are not taken into account in assessing potential health risks.

Coal tar is a complex mixture made when coal is carbonised to make coke or gasified to make coal gas. It contains many of the PAH's from coal and is listed by IARC as a Group 1 mixture, carcinogenic to humans, based on sufficient evidence of human and animal carcinogenicity.[10]

Few of these chemicals, mainly PAH's[12], that can be solublised from coal have been studied and listed as possible carcinogens. Most, including those likely to be the most potent carcinogens, remain untested and therefore are largely not taken into account.

Liberation of Carcinogens by Coal Mining.
Under natural conditions, fossil fuels contribute a relatively small volume of PAHs to the environment. Because most coal and oil deposits are trapped deep beneath layers of rock, there is little chance to emit PAHs to the surface environment. For the first time, CM will allow large amounts of these chemicals to be solublised from coal seams and leached out into ground water, and particulate matter to be released into our atmosphere.

“Safe” levels of Carcinogens.
The dose response curve for the Ames test using varying concentrations of chemical is almost always linear[14] indicating that there is no threshold concentration for mutagenesis. This sCuggests that, as with radiation, there may be no “safe” threshold for chemical mutagens or carcinogens[15,16] and they need to be considered differently to other chemical toxins where a high threshold amount is needed, for example, to adversely affect the function of a whole organ. Chemical carcinogens on the other hand typically initiate cancer by one molecule causing a DNA mutation in one cell. Arguably there is no “safe level” for genotoxic chemicals like PAHs.

Present legislated “safe” or maximum contamination levels are close to the level of detection for the few known carcinogens listed. For example US EPA Maximum Contamination Level (MCL) for benzene in drinking water is 5ng/l .[17] Inhalation carcinogenic potency (WHO air guidence for Europe [28]) for benzo(a)pyrene is four orders of magnitude higher than Benzene:

PAH – benzo(a)pyrene	$8.7x10^{-2}$	unit risk/(µg/cu. m.)
Benzene	$6x10^{-6}$	“ “

ANZECC/ARMCANZ guidelines (1996) specify a concentration limit of 10 ng/L of benzo(a)pyrene in drinking water. This limit has also been adopted by NHMRC. Based on the ratio above the drinking water MCL for benzo(a)pyrene should be several orders of magnitude lower than 10 ng/L.
Typical water testing limits of quantification (LOQ) values for PAHs range from µg/l[18] to 10 ng/l. So testing ground or drinking water may be of little use in determining cancer risk of water contaminated by PAHs.

Assays for Coal Carcinogens.
Testing of nerun-off water is one possible way of detecting carcinogens released from coal by the mining process, as they will be present at higher concentrations when first released from wells. Nearby water supplies and creeks need also to be tested.

ANZECC/ARMCANZ drinking water guidelines (2011) recommends the use of fluorescence detection combined with high performance liquid chromatography (HPLC) provides a sensitive method for PAHs in water (USEPA Draft Method 550, 1990). This method has a detection limit of 29ng/l for Benzo(a)pyrene. It is essential that PAH assays of produce water are carried out routenely at a much lower assay sensitivity, below safe drinking water levels. Stearman *et al* [27] state, “In some instances, the detection level (DL) of some organic compound classes in CSG water may be too high to adequately assess the occurrence of potentially harmful compounds. Aromatic compounds such as BaP have regulatory limits (0.01 µg/L) 50 times less concentrated than the minimum DL of the Bandanna Formation dataset (0.5 µg/L) of this work and the small number of publicly available QLD CSG water organic datasets.” Assays of with detection levels > 3ng/l are needed, so research laboratory methods (Oream *et al* [13] *)* need to be used for routene assays.

Conclusion.
The Australian Institute of Health and Welfare Report[24] on cancer incidence in Australia found that between 1991 and 2009, the number of new cancer cases diagnosed in Australia each year almost doubled; from 66,393 to 114,137. This is likely to be only partly accounted for by increase in population and increased diagnosis; environmental factors are likely to play a major role. Vineis and Xun,[25] describe "The emerging epidemic of environmental cancers in developing countries." Grant[26] has identified air pollutants in particular PAH's as "the likely source of air pollution that affects cancer risk on a large scale, throCMh production of black carbon aerosols with adsorbed polycyclic aromatic hydrocarbons". These types of studies, the recent data on Australian cancer incidence, and the worldwide rise in air- and water-borne chemical carcinogens[29] should be ringing alarm bells throCMhout the public health sector about chemical carcinogens.

As many of the carcinogenic hydrocarbons and PAHs likely to be released by CM are persistent, we need to legislate, and implement the recommendations below, to minimise the release of chemical carcinogens into the atmosphere and groundwater. We need to act now to reduce air and water-borne carcinogens, in order to slow the escalation of chemically induced cancer in future generations.

References.

1. Hanahan, D. and Weinberg, RA. (2011). Hallmarks of cancer: the next generation. Cell *144*, 646-674.
2. Carlo, M. and Croce, MD. (2008). Oncogenes and Cancer . N. Engl. J. Med. *358*, 502-511.
3. Claxton, LD., Umbuzeiro, GDA. and DeMarini, DM. (2010). The Salmonella mutagenicity assay: the stethoscope of genetic toxicology for the 21st century. Environ. Health Perspect. *118*, 1515-1522.
4. OECD. (2006). Detailed review paper on cell transformation assays for detection of chemical carcinogens. DRP No. 31. Fourth draft version.
5. The Carcinogenic potency project. http://toxnet.nlm.nih.gov/cpdb/chemicalsummary.html
6. LERMAN, LS. (1961). Structural considerations in the interaction of DNA and acridines. J. Mol. Biol. *3*, 18-30.
7. Ames, BN., Gurney, EG., Miller, JA. et al. (1972). Carcinogens as frameshift mutagens: metabolites and derivatives of 2-acetylaminofluorene and other aromatic amine carcinogens. Proc. Natl. Acad. Sci. U.S.A. *69*, 3128-3132.
8. Warshawsky, D., Barkley, W. and Bingham, E. (1993). Factors affecting carcinogenic potential of mixtures. Fundam Appl Toxicol *20*, 376-382.
9. Zhao, ZB., Liu, K., Xie, W. et al. (2000). Soluble polycyclic aromatic hydrocarbons in raw coals. J. Hazard. Mater. *73*, 77-85.
10. IARC monograph. *monographs.iarc.fr/ENG/Monographs/vol100F/mono100F-17.pdf*
11. NTN Report Sept 2011: Hydraulic Fracturing in Coal Seam Gas Mining: The Risks to Our Health, Communities, Environment and Climate.
12. Batley, GS., and Kookana, R S., Environmental issues associated with coal seam gas recovery: managing the fracking boom. Environmental Chemistry 9(5) 425-428
13. W. H. Orem, C. A. Tatu, H. E. Lerch, C. A. Rice, T. T. Bartos, A. L. Bates, S. Tewalt, M. D. Corum, Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. Appl. Geochem. 2007, 22, 2240-2256.

14. McCann, J.; Choi, E.; Yamasaki, E.; Ames, B. N. (1975). Detection of carcinogens as mutagens in the Salmonella/microsome test: Assay of 300 chemicals. Proceedings of the National Academy of Sciences of the United States of America **72** (12): 5135–5139.

15. Andrew Teasdale (2011). *Genotoxic Impurities: Strategies for Identification and Control*. Wiley-Blackwell.

16. Tubiana, M. (1992). The carcinogenic effect of exposure to low doses of carcinogens,. British journal of industrial medicine 49 (9): 601–605.

17. *http://water.epa.gov/drink/contaminants/basicinformation*

18. Aligent Technologies Application Note: Determination of 24 PAHs in Drinking Water . *www.chem.agilent.com/Library/applications/5990-7686EN.pdf*

19. Steinzor, N., Subra W., and Sumi, L., (2012) Gas Patch Roulette: How shale gas development Risks Public Health in Pensylvania. http://health.earthworksaction.org

20. McKenzie, LM., Witter, RZ., Newman, LS. et al. (2012). Human health risk assessment of air emissions from development of unconventional natural gas resources. Sci. Total Environ. 424, 79-87.

21. Geralyn Mccarron, Qld GP personal communication.

22. Santos, I., and Maher, D., (2012) Submission to the Dept of Climate Change, *http://www.scu.edu.au/coastal-biogeochemistry/index.php/70/*

23. McDonald, TA. and Komulainen, H. (2005). Carcinogenicity of the chlorination disinfection by-product MX. J Environ Sci Health C Environ Carcinog Ecotoxicol Rev *23*, 163-214.

24. Australian Institute of Health and Welfare . Cancer in Australia an overview 2012 . Cancer Series Number 74. Cat No. CAN 70.

25. Vineis, P. and Xun, W. (2009). The emerging epidemic of environmental cancers in developing countries. Ann. Oncol. *20*, 205-212.

26. Grant, WB. (2009). Air pollution in relation to U.S. cancer mortality rates: an ecological study; likely role of carbonaceous aerosols and polycyclic aromatic hydrocarbons. Anticancer Res. 29, 3537-3545.

27. Stearman, W , Taulis, M, Smith, J, and Corkeron, M, (2014). Assessment of Geogenic Contaminants in Water Co-Produced with Coal Seam Gas Extraction in Queensland, Australia: Implications for Human Health Risk. Geosciences 2014, 4, 219-239.

28. Air Quality. Guidelines for Europe. (20000) World Health Organization. Regional Office forEurope. Copenhagen. WHO Regional Publications, European Series, No. 91.