#### TEDX

The Endocrine Disruption Exchange P.O. Box 1407, Paonia, CO 81428 970-527-4082 www.endocrinedisruption.org tedx@tds.net

# **INTRODUCTION**

The following summary is based on an analysis of the potential health effects of products and chemicals used during natural gas operations. The names and possible health effects of the products and chemicals summarized below are available in an Excel spreadsheet for easy sorting and searching.\* Note that this is not a complete list of products and chemicals used in natural gas operations.

# **METHODS:** What we did

### Data sources

Acquiring information about the products and chemicals used in natural gas operations continues to be extremely difficult. TEDX has spent several years collecting data from a variety of sources including state Emergency Planning and Community Right-to-Know Act (EPCRA) Tier II reports, Environmental Impact Statement and Environmental Assessment Statement disclosures, rule-making documents, accident and spill reports, the U.S. Bureau of Land Management, the U.S. Forest Service, state agencies, non-profit organizations, and the natural gas industry.

For nearly every product identified, Material Safety Data Sheets (MSDSs) were acquired, with the exception of a few that came from state Tier II Reports. MSDSs are designed to inform those who handle, ship, and use products that contain toxic chemicals about their physical and chemical characteristics, and their direct and/or immediate health effects, in order to prevent injury while working with the products. The sheets are also designed to inform emergency response crews in case of accidents or spills. Many MSDSs do not address the outcome of long term, intermittent or chronic exposures, or adverse health effects that may not be expressed until years after the exposure. The Occupational Safety and Health Administration (OSHA) requires product manufacturers to include certain elements in MSDSs, but they are not required to submit them to OSHA for approval before attaching them to their products. Thus, accuracy and completeness are entirely up to the company that produces the MSDS.

MSDSs can be lacking in information in many ways. The majority of MSDSs do not disclose 100% of the product composition. They also list non-specific ingredients, such as "surfactant" or "biocide" that describe the function of the ingredient but do not specify the ingredient name. Other vague words that are used include: proprietary, mixture, unspecified, various, unregulated, or no hazardous ingredients. The most specific way to identify chemical ingredients is by using CAS numbers. The American Chemical Society developed the CAS (Chemical Abstract Service) number system using unique number sequences to identify chemical elements, compounds, isomers of chemicals, polymers, biological sequences, or mixtures. CAS numbers provide a universal identity to substances that can be known by different names.

## Health Effects

Only chemicals with CAS numbers could be accurately investigated for their health effects. Information about the potential health effects of each chemical with a CAS number was obtained from these sources:

- Material Safety Data Sheets
- Publicly available government databases:
  - o TOXNET
  - o Hazardous Substances Database
- Published scientific studies (located through PubMed and Web of Science)

Information was often limited because of the lack of published research on many products, including industry laboratory studies submitted to EPA for registration but classified as confidential business information.

Health effect data were organized into 14 health categories, focusing on the main organs and systems that are identified on MSDSs, government toxicological reports, and in the medical literature. The categories encompass all seven priority health conditions identified by the Agency for Toxic Substances and Disease Registry. For our summary analysis we subsumed developmental and reproductive health effects under the category for endocrine disruption, resulting in 12 categories. The 12 health effect categories are: skin, eye and sensory organ; respiratory; gastrointestinal and liver; brain and nervous system; immune; kidney; cardiovascular and blood; cancer; mutagenic; endocrine disruption; other; and ecological effects.

# Data Analysis

The products, the chemicals they contain, and their health effects were entered into an Excel spreadsheet. We also entered data indicating what percentage of each product was disclosed in the MSDS. Then, using only the chemicals that had a CAS number, we produced a profile based on how many chemicals showed evidence of potential health effects in each of the 12 categories. We also created separate profiles for the water soluble chemicals and volatile chemicals.

# **RESULTS: What we learned**

### Product composition disclosure

Products may contain more than one chemical, and a given chemical may occur in more than one product. Our spreadsheet currently contains 980 products. For 421 of the 980 products (43%), less than 1% of the total composition of the product was reported on the MSDS (Figure 1). Less than 50% of the composition was reported for 136 products (14%), and between 51% and 95% of the composition was reported for 291 (30%) of the products. Only 133 products (14%) had information on more than 95% of their full composition.



For each product, we totaled the number of health effects of the chemicals in that product. Figure 2 shows that 10% of the products had no health effects, while 90% had at least one potential health effect. Nearly half of the products (47%) contained one or more chemicals considered to be endocrine disruptors, which are chemicals that interfere with the endocrine system, including development and reproduction.



## Chemical summary

In the 980 products identified above, there were a total of 649 chemicals. Specific chemical names and CAS numbers could not be determined for 286 (44%) of the chemicals, therefore, the health effects summary is based on the remaining 362 chemicals with CAS numbers. Figure 3 shows percentages of the 362 chemicals that were found to be associated with effects in each of the 12 health effect categories. Note that many chemicals have health effects, respiratory effects and gastrointestinal or liver effects. The brain and nervous system can be harmed by 55% of the chemicals. These four health effect categories (on the left side of the figure) are likely to appear immediately or soon after exposure. They include symptoms such as burning eyes, rashes, coughs, sore throats, asthma-like effects, nausea, vomiting, headaches, dizziness, tremors, and convulsions. Other effects, including cancer, organ damage, and harm to the endocrine system, may not appear for months or years later. Between 22% and 47% of the chemicals were associated with these possibly longer-term health effects. Forty-eight percent of the chemicals have health effects in the category labeled 'Other'. The 'Other' category includes such effects as changes in weight, or effects on teeth or bones, for example, but the most often cited effect in this category is the ability of the chemical to cause death.



Figure 4 breaks out the health effects by pathway of exposure. A total of 210 chemicals (58%) are water soluble while 131 chemicals (36%) are volatile; in other words, they can become airborne. Of these volatile chemicals over 93% can harm the eyes, skin, sensory organs, respiratory tract, gastrointestinal tract or liver. Compared with the soluble chemicals, far more of these chemicals (86%) can cause harm to the brain and nervous system. Seventy-two percent of the volatile chemicals can harm the cardiovascular system and blood, and 66% can harm the kidneys. Overall, the volatile chemicals produce a different profile with higher percentages than the water soluble chemicals. Because they can be inhaled, swallowed, and also reach the skin, the potential for exposure to volatile chemicals is greater.



Appendix A provides a list of the chemicals with CAS numbers found in the highest number of products and their associated number of health effects, to assist in prioritizing the chemicals to be monitored.

## DISCUSSION: What we have to say about it

Clearly, many of the products and chemicals used by the natural gas industry are not benign. As the industry continues to expand and tap into additional natural gas formations, the list of products will grow. New products and chemicals continue to be introduced into the market as a result of increasing competition among those who manufacture and sell products; and product specialization to address the geology and varying geochemical conditions of natural gas formations.

Without full knowledge of what products and chemicals are being used, it is extremely difficult to know what air and water quality tests to conduct. Appendix A displays the chemicals that appear in the highest number of products, along with the number of health effects of each chemical. Although this does not necessarily equate to the most frequently used chemicals at any given time or location, it can provide some guidance in developing air and water quality monitoring protocols. Regular air and water quality monitoring in and around natural gas development should become standard procedure that includes baseline monitoring prior to new wells being developed. For those living near natural gas development, measurable changes in air quality will take place well before changes in drinking water quality. In addition to the chemicals introduced during drilling and fracturing, air quality monitoring should target the numerous volatile, naturally occurring, toxic chemicals found underground that may also be released during the process.

Of note is that 47% of the products have the potential to affect the endocrine system, including human and wildlife development and reproduction. The endocrine system is the exquisitely balanced system of glands and hormones that regulates such vital functions as body growth, response to stress, sexual development and

behavior, production and use of insulin, rate of metabolism, intelligence and behavior, and the ability to reproduce. The endocrine system operates at very low concentrations of hormones, often in parts-per-billion or less, making it susceptible to very low levels of exposure, which can impact organisms and their offspring, including humans. Prenatal exposure should especially be avoided. Endocrine disrupting effects include reduced sperm production, infertility, hormone imbalances, effects on the thyroid, adrenals, pituitary, and more. Effects like these might not be seen for months or years and would be difficult to trace back to exposure to gas industry chemicals.

For over seven years, environmental and public health advocates have called for full product disclosure of drilling and fracking chemicals. After a nurse became critically ill while attending a laborer involved in a fracking accident, and the attending physicians could not find out what she was exposed to, the real urgency for full disclosure became apparent. In 2008 Colorado passed a rule (the first of its kind) that upon request through the Colorado Oil and Gas Conservation Commission, operators must disclose product ingredients to victims or their physicians in case of an accident. Unfortunately, the response to such a request could take several days, long after it could be of any assistance for emergency diagnosis and treatment. In 2010, Wyoming became the first state to require publicly available disclosure of chemicals in fracking products, including the volumes or quantity of chemicals used. Already Wyoming is receiving requests for proprietary status which would prevent public disclosure of a number of fracking products.

These efforts are a good start, but there is much more information that needs to be disclosed fully and publicly. Each drilling and fracturing event is custom-designed depending on the geology, depth and resources available. The chemicals and products used and the amounts or volumes used can differ from well to well. Complete records for each well must be kept for an accurate accounting of what is being introduced into watersheds, air, and soil. This information should include the exact location of the well; the complete composition of the fluids injected underground, including the complete formulation, weight and volume of every product and chemical used; the depths and pressures at which material/mixtures were injected; the amount and composition of the recovered liquids; and their disposal method and location.

However, while the drilling and fracking contractors can be required to tell everything they know about a product, they largely rely on MSDSs from the product manufacturers. As our analysis indicates, many MSDSs provide information on only a fraction of the full product ingredients. There will not be true full disclosure until the *product manufacturers* divulge 100% of the chemical ingredients in their products. It is time for those charged with protecting public health and the environment to demand full disclosure directly from the natural gas products industry. Additionally, responsible drilling and fracking companies should be insisting on safer products from their suppliers to protect the health of their employees and reduce their liability. Most importantly, the industry needs to assure its drilling and fracking fluids and toxic byproducts are retained in closed-loop production systems that prevent the release of any toxic chemicals into the ambient environment.

For a more in-depth discussion of these issues, read our manuscript "Natural Gas Operations from a Public Health Perspective" accepted for publication in the *International Journal of Human and Ecological Risk Assessment*.

\*To download the database of products, chemicals and health effects in an Excel spreadsheet; a PDF of this Summary Statement; and our manuscript "Natural Gas Operations from a Public Health Perspective" go to <u>http://www.endocrinedisruption.com/chemicals.multistate.php</u>.

### Appendix A. Chemicals found in the highest number of products

Chemical	CAS #	Number of Products	Number of Health effects
Crystalline silica, quartz	14808-60-7	124	7
Methanol	67-56-1	76	11
Isopropanol (Propan-2-OL)	67-63-0	50	10
Petroleum distillate hydrotreated light	64742-47-8	24	6
(2-BE) Ethylene glycol monobutyl ether	111-76-2	23	11
Bentonite	1302-78-9	20	6
Diesel 2	68476-34-6	20	10
Naphthalene	91-20-3	19	12
Ethylene glycol	107-21-1	18	10
Aluminum oxide	1344-28-1	17	3
Sodium hydroxide	1310-73-2	17	5
Barite (BaSO4)	7727-43-7	15	5
Heavy aromatic petroleum naphtha (aromatic solvent)	64742-94-5	15	5
Sodium chloride	7647-14-5	15	9
Crystalline silica, cristobalite	14464-46-1	14	5
Mica	12001-26-2	14	3
Crystalline silica, tridymite	15468-32-3	13	3
Hydrochloric acid (HCl)	7647-01-0	13	7
Xylene	1330-20-7	12	10
Glutaraldehyde	111-30-8	11	11
Guar gum	9000-30-0	10	3
Iron oxide (Fe203, Diiron trioxide)	1309-37-1	10	4
Potassium chloride	7447-40-7	10	8
Potassium hydroxide	1310-58-3	10	7
Xanthan gum	11138-66-2	10	4
Fuel oil #2	68476-30-2	9	11
Hydrotreated heavy petroleum naphtha	64742-48-9	9	8
Limestone (Calcium carbonate)	1317-65-3	9	3
Sodium carboxymethylcellulose ( <i>Polyanionic cellulose</i> )	9004-32-4	9	5
Butanol (N-butyl alcohol, Butan-1-OL, 1-Butanol)	71-36-3	8	8
Calcium hydroxide	1305-62-0	8	8
Crystalline silica (silicon dioxide)	7631-86-9	8	4
Ethanol (Acetylenic alcohol)	64-17-5	8	12
Formic acid	64-18-6	8	11
Graphite	7782-42-5	8	4
2-Ethylhexanol	104-76-7	7	11
Acetic acid	64-19-7	7	9
Ammonium bisulfate	10192-30-0	7	6
Asphaltite (Gilsonite, Hydrocarbon black solid)	12002-43-6	7	4
Calcium chloride	10043-52-4	7	8
Ethylbenzene	100-41-4	7	11
Ethoxylated nonvlphenol	9016-45-9	7	6
Petroleum distillate naphtha	8002-05-9	7	12
Polyacrylamide/polyacrylate copolymer (Copolyer of acrylamide & sodium acrylate, partially hydrolyzed polyacrylalmide)	25085-02-3	7	3
Propargyl alcohol (Prop-2-YN-1-OL)	107-19-7	7	9
Tetramethylammonium chloride	75-57-0	7	8