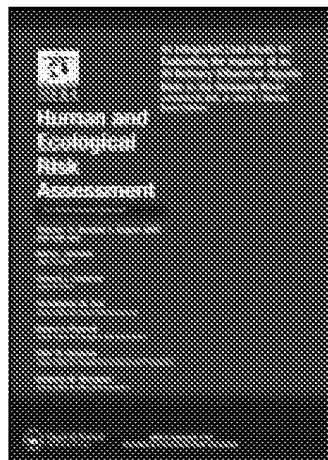


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Natural Gas Operations from a Public Health Perspective

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Hazard Assessment Articles

Natural Gas Operations from a Public Health Perspective

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ABSTRACT

The technology to recover natural gas depends on undisclosed types and amounts of toxic chemicals. A list of 944 products containing 632 chemicals used during natural gas operations was compiled. Literature searches were conducted to determine potential health effects of the 353 chemicals identified by Chemical Abstract Service (CAS) numbers. More than 75% of the chemicals could affect the skin, eyes, and other sensory organs, and the respiratory and gastrointestinal systems. Approximately 40–50% could affect the brain/nervous system, immune and cardiovascular systems, and the kidneys; 37% could affect the endocrine system; and 25% could cause cancer and mutations. These results indicate that many chemicals used during the fracturing and drilling stages of gas operations may have long-term health effects that are not immediately expressed. In addition, an example was provided of waste evaporation pit residuals that contained numerous chemicals on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Emergency Planning and Community Right-to-Know Act (EPCRA) lists of hazardous substances. The discussion highlights the difficulty of developing effective water quality monitoring programs. To protect public health we recommend full disclosure of the contents of all products, extensive air and water monitoring, coordinated environmental/human health studies, and regulation of fracturing under the U.S. Safe Drinking Water Act.

Key Words: drilling, health, hydraulic fracturing, natural gas, ozone, pollution.

INTRODUCTION

Over the past two decades, in an effort to reduce dependence on imported fossil fuels, the U.S. government has supported increased exploration and production of

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natural gas. The responsibility for overseeing the nation's underground minerals lies with the U.S. Department of Interior, Bureau of Land Management (BLM) with some oversight from the U.S. Environmental Protection Agency (USEPA). Attempting to meet the government's need for energy self-sufficiency, the BLM has auctioned off thousands of mineral leases and issued permits to drill across vast acreages in the U.S. Rocky Mountain West. Since 2003, natural gas operations have increased substantially, with annual permits in Colorado alone increasing from 2,249 to 8,027 in 2008 (Colorado Oil and Gas Conservation Commission 2010).

In tandem with federal support for increased leasing, legislative efforts have granted exclusions and exemptions for oil and gas exploration and production from a number of federal environmental statutes, including the Clean Water Act, the Clean Air Act, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, better known as the Superfund Act), the Resource Conservation and Recovery Act (RCRA), the Toxic Release Inventory under the Emergency Planning and Community Right-to-Know Act (EPCRA), and the National Environmental Policy Act (NEPA) (Oil and Gas Accountability Project 2007). The most recent of these efforts was an amendment included in the 2005 Energy Policy Act that prevented the use of the Safe Drinking Water Act to regulate certain activities, known as hydraulic fracturing, which are involved in 90% of natural gas drilling.

The cumulative effect of these exemptions and exclusions has been to create a federal void in environmental authority over natural gas operations, leaving the responsibility primarily up to the states. Although some states have oil and gas commissions to watch over natural gas production activity, the primary mission of these agencies has been to facilitate natural gas extraction and increase revenues for the states. In addition, when states issue permits to drill, they have not traditionally required an accounting of how the resulting liquid and solid waste would be handled. In short, their focus has not typically been on health and the environment.

The Need for Chemicals

In keeping with the rush to produce more natural gas, technological advances have permitted the industry to drill deeper and expand wider, tapping into gas reserves with greater facility and profitability. While these advances have allowed the mining of vast, newly discovered gas deposits, the new technology depends heavily on the use of undisclosed types and amounts of toxic chemicals.

Chemicals are used throughout operations to reach and release natural gas. First, combinations of chemicals are added to the "muds" used to drill the bore hole. Chemicals are added to increase the density and weight of the fluids in order to facilitate boring, to reduce friction, to facilitate the return of drilling detritus to the surface, to shorten drilling time, and to reduce accidents. After drilling, hydraulic fracturing (also known as fracking, frac'ing, or stimulation) is done to break up the zone in which the gas is trapped and make it easier for the gas to escape, increasing a well's productivity. In the U.S. West, approximately a million or more gallons of fluid containing toxic chemicals are injected underground during this operational stage. As with drilling, chemicals are used in fracking fluids for many purposes (Table 1). One well can be fracked 10 or more times and there can be up to 30 wells on one pad. An estimated 10% to 90% of the fracking fluid is returned to the surface during

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Table 1. Functional categories of hydraulic fracturing chemicals.

| | |
|----------------------|--|
| Acids | To achieve greater injection ability or penetration and later to dissolve minerals and clays to reduce clogging, allowing gas to flow to the surface. |
| Biocides | To prevent bacteria that can produce acids that erode pipes and fittings and break down gellants that ensure that fluid viscosity and proppant transport are maintained. Biocides can produce hydrogen sulfide (H ₂ S) a very toxic gas that smells like rotten eggs. |
| Breakers | To allow the breakdown of gellants used to carry the proppant, added near the end of the fracking sequence to enhance flowback. |
| Clay stabilizers | To create a fluid barrier to prevent mobilization of clays, which can plug fractures. |
| Corrosion inhibitors | To reduce the potential for rusting in pipes and casings. |
| Crosslinkers | To thicken fluids often with metallic salts in order to increase viscosity and proppant transport. |
| Defoamers | To reduce foaming after it is no longer needed in order to lower surface tension and allow trapped gas to escape. |
| Foamers | To increase carrying-capacity while transporting proppants and decreasing the overall volume of fluid needed. |
| Friction reducers | To make water slick and minimize the friction created under high pressure and to increase the rate and efficiency of moving the fracking fluid. |
| Gellants | To increase viscosity and suspend sand during proppant transport. |
| pH control | To maintain the pH at various stages using buffers to ensure maximum effectiveness of various additives. |
| Proppants | To hold fissures open, allowing gas to flow out of the cracked formation, usually composed of sand and occasionally glass beads. |
| Scale control | To prevent build up of mineral scale that can block fluid and gas passage through the pipes. |
| Surfactants | To decrease liquid surface tension and improve fluid passage through pipes in either direction. |

well completion and subsequent production (BC Oil and Gas Commission 2010; New York State Department of Environmental Conservation Division of Mineral Resources 2009), bringing with it toxic gasses, liquids, and solid material that are naturally present in underground oil and gas deposits. Under some circumstances, none of the injected fluid is recovered.

In most regions of the country, raw natural gas comes out of the well along with water, various liquid hydrocarbons including benzene, toluene, ethylbenzene, and xylene (as a group, called BTEX), hydrogen sulfide (H₂S), and numerous other organic compounds that have to be removed from the gas. When the gas leaves the well it is passed through units called heater treaters that are filled with triethylene glycol and/or ethylene glycol that absorbs the water from the gas. Once the glycol solution becomes saturated with water, the heaters turn on and raise the temperature enough to boil off the water, which is vented through a closed system

and upon cooling, ends up in a nearby tank labeled “produced water.” The glycol fluid, which has a higher boiling point than water, cools and is reused. During the heating process at critical temperatures the oily substances that came up with the gas become volatile and then re-condense into a separate holding tank. This is known as “condensate” water. The contaminated water can be re-injected underground on the well pad or off site, common practices in the eastern United States, or hauled off the well pad to waste evaporation pits in the U.S. West. Temporary pits are also constructed during drilling to hold the cuttings, used drilling mud which is often re-used, and any other contaminated water that comes to the surface while drilling. These reserve pits on well pads are supposed to be drained and covered with top soil or other suitable material within a month after drilling stops.

An Unexpected Side Effect: Air Pollution

In addition to the land and water contamination issues, at each stage of production and delivery tons of toxic volatile compounds (VOCs), including BETX, other hydrocarbons, and fugitive natural gas (methane), can escape and mix with nitrogen oxides (NOx) from the exhaust of diesel-fueled, mobile, and stationary equipment, to produce ground-level ozone (CH2MHILL 2007; Colorado Department of Public Health and Environment [CDPHE] 2007; URS 2008; U.S. Congress, Office of Technology Assessment 1989). One highly reactive molecule of ground level ozone can burn the deep alveolar tissue in the lungs, causing it to age prematurely. Chronic exposure can lead to asthma and chronic obstructive pulmonary disease (COPD), and is particularly damaging to children, active young adults who spend time outdoors, and the aged (Islam *et al.* 2007; Tager *et al.* 2005; Triche *et al.* 2006). Ozone combined with particulate matter less than 2.5 micrometers produces smog (haze) that has been demonstrated to be harmful to humans as measured by emergency room admissions during periods of elevation (Peng *et al.* 2009). Gas field ozone has created a previously unrecognized air pollution problem in rural areas, similar to that found in large urban areas, and can spread up to 200 miles beyond the immediate region where gas is being produced (U.S. Congress, Office of Technology Assessment 1989; Roberts 2008). Ozone not only causes irreversible damage to the lungs, it is similarly damaging to conifers, aspen, forage, alfalfa, and other crops commonly grown in the western United States (Booker *et al.* 2009; Reich 1987; U.S. Congress, Office of Technology Assessment 1989). Adding to this air pollution is the dust created by fleets of diesel trucks working around the clock hauling the constantly accumulating condensate and produced water to large waste facility evaporation pits on unpaved roads. Trucks are also used to haul the millions of gallons of water from the source to the well pad.

PROJECT DESIGN

The following project grew from a year 2004 request by OGAP (Oil and Gas Accountability Project) to TEDX (The Endocrine Disruption Exchange) to explore the potential health effects of chemicals used during drilling, fracking, processing, and delivery of natural gas. OGAP, a project of Earthworks, is a national non-profit

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organization established in 1999 to watchdog the oil and natural gas industry. TEDX is a non-profit organization dedicated to compiling and disseminating technical information on chemicals that affect health and the environment.

Data Sources

In order to find out what chemicals were being used to extract natural gas, we took advantage of the information on the Material Safety Data Sheets (MSDSs) that accompany each product used during natural gas operations. MSDSs detailing specific products in use were provided by multiple sources including the BLM, U.S. Forest Service, state government departments, and the natural gas industry. MSDSs are designed to inform those who handle, ship, and use products that contain dangerous chemicals. They provide information about the physical and chemical characteristics of the chemicals in a product, and the immediate and chronic health effects, in order to prevent injury while working with the products. They are also designed to inform emergency response crews in case of accidents or spills. In addition to the MSDSs, we also used State Tier II Reports that must be filed by storage facilities under EPCRA. This Act sets a minimum amount above which a product that contains a hazardous substance in a storage facility has to be reported. We also supplemented our analysis with product information from disclosures in Environmental Impact Statements, Environmental Assessment Statements, and accident and spill reports. At first we looked only at what was taking place in Colorado and over the course of several years we acquired information from Wyoming, New Mexico, Texas, Washington, Montana, Pennsylvania, and New York. The list of products and chemicals quickly grew, making it apparent that hundreds of different products serving many purposes were being used in natural gas operations across the country. The number of chemical products manufacturers has also grown, making this a highly competitive industry.

It should be clear that our list of products is not complete, but represents only products and chemicals that we were able to identify, through a variety of sources, as being used by industry during natural gas operations. For most products, we cannot definitively say whether they were used during drilling or during fracking. However, an accidental blow-out of the Crosby well in Wyoming provided a unique opportunity to analyze the chemicals used during drilling, as fracking had not yet begun on that well. When the blow-out occurred, methane and other gases, petroleum condensates, and drilling fluids (muds) were released from fissures in the ground adjacent to the well. During the 58 hours the eruption took place, 25,000 square feet of soil surface in the area were contaminated. The driller released copies of the MSDSs for the products used during the blow-out and later we found the names of several more products from remedial action work plans to clean up the site (Terracon 2007).

On another occasion we were provided data from a 2007 New Mexico study, sponsored by 19 oil and gas companies and conducted by a third party consultant and analytical laboratory. This gave us the opportunity to explore the health effects of chemicals in samples of pit solids drawn from six evaporation pits where gas operations were ceasing.

Data Limitations

MSDSs and Tier II reports are fraught with gaps in information about the formulation of the products. The U.S. Occupational Safety and Health Administration (OSHA) provides only general guidelines for the format and content of MSDSs. The manufacturers of the products are left to determine what information is revealed on their MSDSs. The forms are not submitted to OSHA for review unless they are part of an inspection under the Hazard Communication Standard (U.S. Department of Labor 1998). Some MSDSs report little to no information about the chemical composition of a product. Those MSDSs that do may only report a fraction of the total composition, sometimes less than 0.1%. Some MSDSs provide only a general description of the content, such as “plasticizer,” “polymer,” while others describe the ingredients as “proprietary” or just a chemical class. Under the present regulatory system all of the above “identifiers” are permissible. Consequently, it is not surprising that a study by the U.S. General Accounting Office (1991) revealed that MSDSs could easily be inaccurate and incomplete.

Tier II reports can be similarly uninformative, as reporting requirements vary from state to state, county to county, and company to company. Some Tier II forms include only a functional category name (*e.g.*, “weight materials” or “biocides”) with no product name. The percent of the total composition of the product is rarely reported on these forms.

The most critical limiting factor in our research was that Chemical Abstract Service (CAS) numbers were often not provided on MSDSs. The American Chemical Society has established the CAS number system to identify unique chemical substances. A single substance can have many different names, but only one CAS number. CAS numbers identify substances that may be a single chemical, an isomer of a chemical, a mixture of isomers, polymers, biological sequences, or a mixture of related chemicals. For purposes of accuracy, our research into the health effects of chemicals used in natural gas operations was restricted to only chemicals for which a CAS number was available.

Health Effects

Information on the health effects associated with identified chemicals was obtained from MSDSs, as well as government toxic chemical databases such as TOXNET and the Hazardous Substances Database, and through literature searches of biomedical studies. Information available for some chemicals is limited due to lack of access to studies performed on the toxicity of the substance. For example, many laboratory studies submitted to USEPA for the registration of chemicals are not accessible on the basis that the information is proprietary to the industry.

Health effects were divided into 14 health categories, focusing on the main target organs or systems that are identified on MSDSs, government toxicological reports, and in medical literature. The categories include all seven priority health conditions identified by the Agency for Toxic Substances and Disease Registry (ATSDR 2010) associated with uncontrolled hazard waste sites listed as required by CERCLA, 1984, as amended (U.S. Environmental Protection Agency 1984). We reduced these to 12 categories by combining developmental and reproductive health impacts under endocrine disruption. The resulting 12 categories included: skin, eye and sensory

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organ, respiratory, gastrointestinal and liver, brain and nervous system, immune, kidney, cardiovascular and blood, cancer, mutagenic, endocrine disruption, other, and ecological effects.

Data Analysis

Using the data sources described earlier, we entered the names of all the products and chemicals into a spreadsheet. Initially, chemicals were separated according to the state in which the data source originated. Analysis of the profiles of health effects revealed minimal differences across states, thus for this report we combined all the data into one multi-state analysis. Using only the chemicals on the multi-state list for which CAS numbers were available, we produced a profile based on how often each of the 12 possible health effects were associated with the chemicals. We created separate profiles for the water soluble chemicals alone, and the volatile chemicals alone. We also did an analysis of the drilling chemicals from the Wyoming well-blowout and an analysis of the chemicals found in the New Mexico evaporation pits. Finally, we tested the utility of the spreadsheet for providing guidance for water quality monitoring, focusing on the most potentially harmful and frequently used chemicals. The spreadsheet is available at <http://www.endocrinedisruption.org/chemicals.multistate.php>.

RESULTS

Product Information

As of May, 2010, TEDX identified 944 products used in natural gas operations in the United States. Of these, between 95 and 100% of the ingredients were available for 131 (14%) of the products (Figure 1). For 407 (43%) of the products, less than 1% of the total product composition was available. For many of those 407 products, only the name of the product with no identifiable chemical name or percent composition was reported. A total of 632 chemicals were reported in the products and we were able to locate CAS numbers for 353 (56%) of them.

Health Effects Profile

Using the health effect information for the 353 chemicals with CAS numbers, we created a profile of possible health effects that depicts the percentage of chemicals associated with each of the 12 health effect categories (Figure 2). Viewing the profile from left to right, more than 75% of the chemicals on the list can affect the skin, eyes, and other sensory organs, the respiratory system, the gastrointestinal system, and the liver. More than half the chemicals show effects on the brain and nervous system. These first four categories represent effects that would likely be expressed upon immediate exposure, such as eye and skin irritation, nausea and/or vomiting, asthma, coughing, sore throat, flu-like symptoms, tingling, dizziness, headaches, weakness, fainting, numbness in extremities, and convulsions. Products containing chemicals in powder form, irritants, or highly corrosive and volatile chemicals would all come with MSDS warnings in one or more of these categories. In all probability, none of the chemicals in these categories would normally be ingested during natural

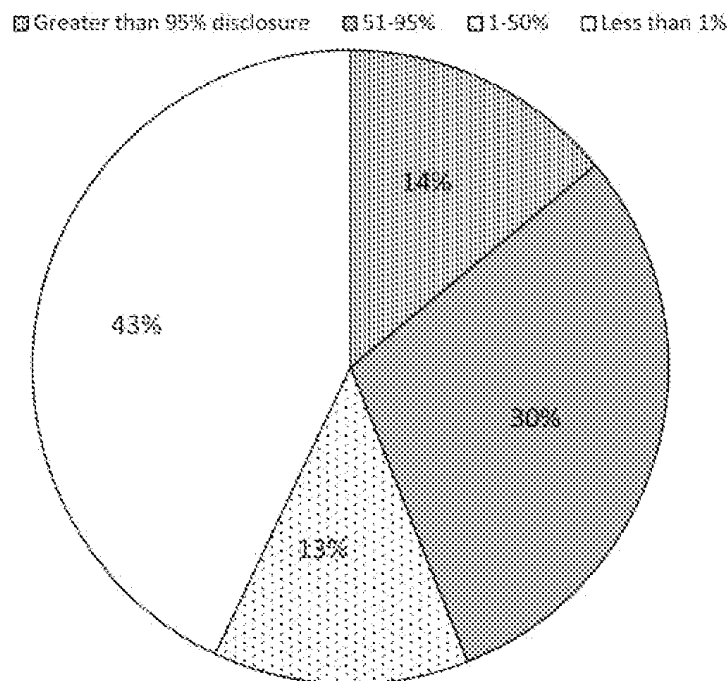


Figure 1. Percent of composition disclosed for 944 products used in natural gas operations.

gas operations, but immediate eye, nasal, dermal contact, and inhalation could lead to rapid absorption and cause direct exposure to the brain and other vital organ systems.

Health categories that reflect chronic and long-term organ and system damage comprise the middle portion of Figure 2. These include the nervous system (52%), immune system (40%), kidney (40%), and the cardiovascular system and blood (46%). More than 25% of the chemicals can cause cancer and mutations. Notably, 37% of the chemicals can affect the endocrine system that encompasses multiple organ systems including those critical for normal reproduction and development. The category of “other” is more common, and includes effects on weight, teeth, and bone and the ability of a chemical to cause death. More than 40% of the chemicals have been found to have ecological effects, indicating that they can harm aquatic and other wildlife.

Volatile and Soluble Chemicals

Separate health category profiles are shown in Figure 3 for the volatile and water soluble chemicals. Approximately 37% of the chemicals are volatile and can become airborne. More than 89% of these chemicals can harm the eyes, skin, sensory organs, respiratory tract, gastrointestinal tract, or liver. Compared with the soluble chemicals, far more of the volatile chemicals (81%) can cause harm to the brain and nervous system. Seventy one percent of the volatile chemicals can harm the cardiovascular system and blood, and 66% can harm the kidneys. Overall, the volatile chemicals produce a profile that displays a higher frequency of health effects than the water soluble chemicals. In addition, because they vaporize, not only can

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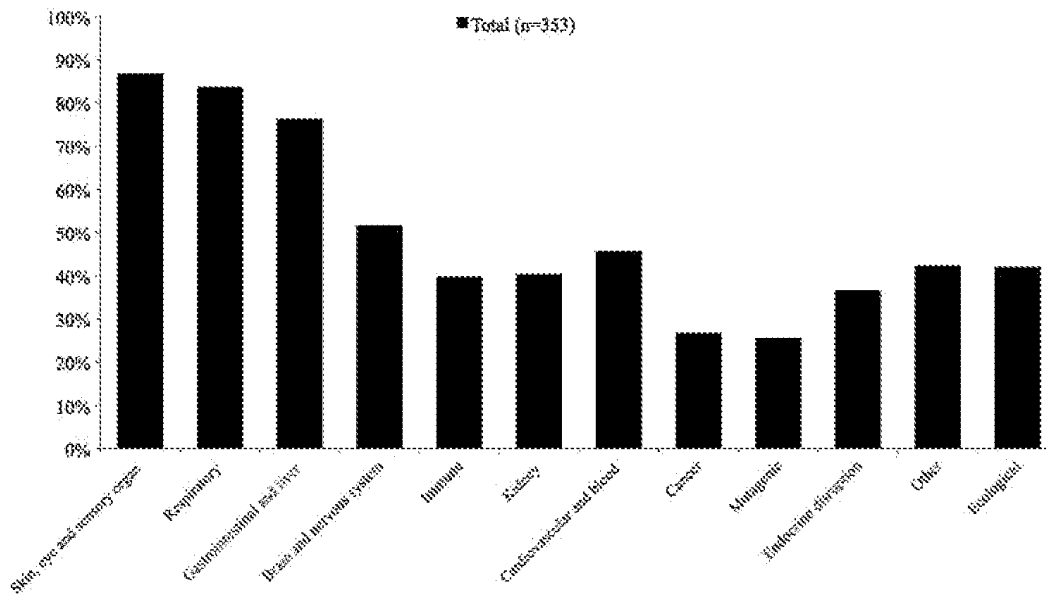


Figure 2. Profile of possible health effects of chemicals with CAS numbers used in natural gas operations.

they be inhaled, but also ingested and absorbed through the skin, increasing the chance of exposures.

Drilling Chemicals

The profile for the 22 drilling chemicals identified from the well blow-out in Wyoming are shown in Figure 4. The profile was unique in the following ways. All

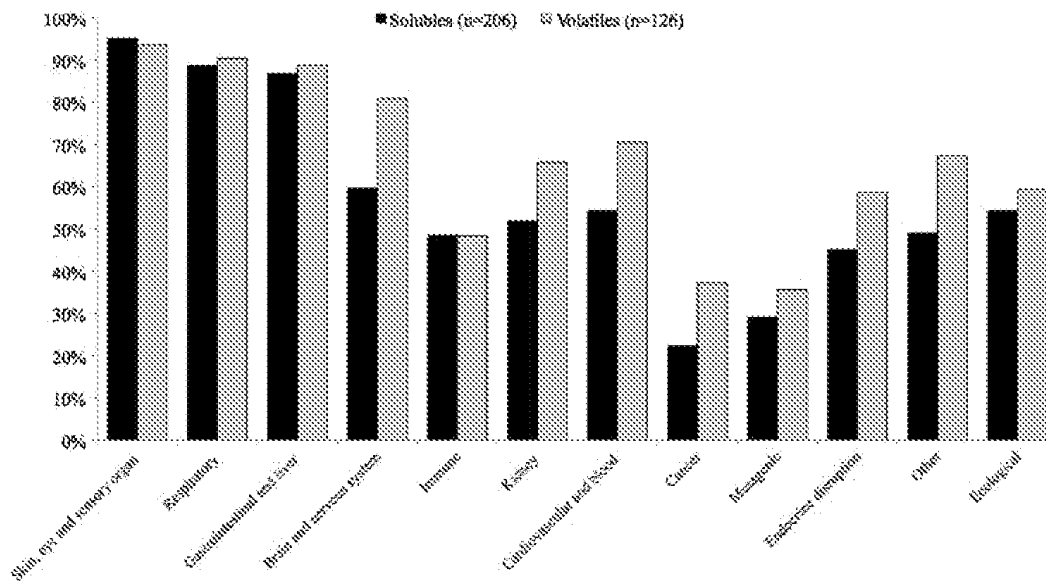


Figure 3. Profile of possible health effects of soluble and volatile chemicals with CAS numbers used in natural gas operations.

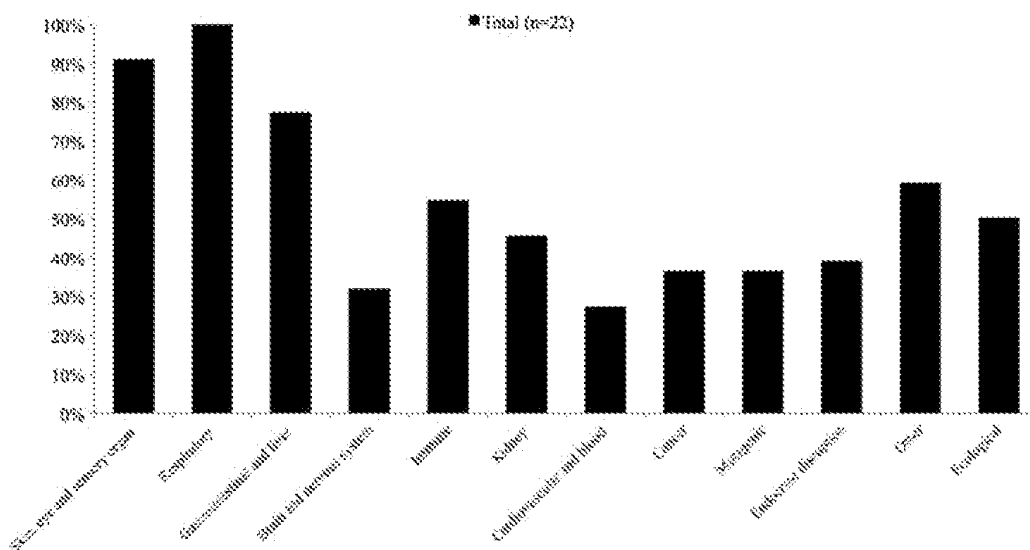


Figure 4. Profile of possible health effects of chemicals with CAS numbers used to drill the Crosby 25-3 well, Wyoming.

the chemicals used in the drilling fluids were associated with respiratory effects. Nearly 60% were associated with “other” effects, a category that includes outright mortality as an end point. A relatively high percentage of chemicals that affect the immune system were used.

Evaporation Pit Chemicals

Shown in Figure 5 are the health effects of the 40 chemicals and metals reported in the New Mexico evaporation pits. These chemicals produced a health profile even

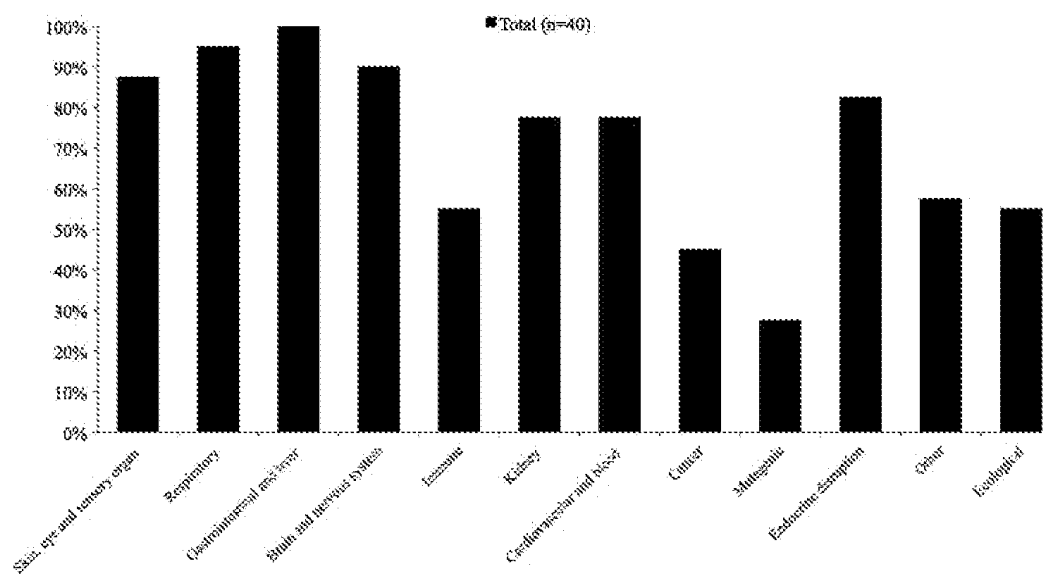


Figure 5. Profile of possible health effects of chemicals with CAS numbers found in six New Mexico drilling evaporation pits.

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more hazardous than the pattern produced by the drilling and fracking chemicals. Upon further investigation, we discovered that 98% of the 40 chemicals found in the pits are listed on USEPA's 2005 CERCLA (Superfund) list and 73% are on the 2006 EPCRA List of Lists of reportable toxic chemicals. Of the nine chemicals found to exceed the New Mexico state limits, all are on the CERCLA list and all but one are on the EPCRA List of Lists.

Analyses for Water Quality Monitoring

For the purpose of water quality monitoring guidance, we analyzed the data according to the most potentially harmful chemicals and the most frequently used chemicals. In Table 2 is provided a list of the most egregious chemicals, those with 10 or more health effects. Roughly half of these chemicals are used in only one product on our list, making it impractical and a waste of time and money to try to test water for the most harmful chemicals. A more practical approach would be to test for the most frequently used chemicals. Although we do not know how often each product is used, we assume that the more products that contain a given chemical, the more likely it is to be detected in a water sample. Shown in Table 3 are all the chemicals on our list that were found in at least seven different products. Many of these chemicals are relatively harmless. The most frequently cited chemical was crystalline silica (quartz), which was reported in 125 different products. Note that petroleum distillates and a variety of alcohols are found in numerous products, as are several forms of potassium, which is a relatively easy and inexpensive chemical to detect in water. This list may prove useful in devising a water monitoring program. Regardless of how many health effects a chemical has, elevated levels of frequently used chemicals found in a water source could provide evidence of communication between natural gas operations and water resources.

DISCUSSION

Industry representatives have said there is little cause for concern because of the low concentrations of chemicals used in their operations. Nonetheless, pathways that could deliver chemicals in toxic concentrations at less than one part-per-million are not well studied and many of the chemicals on the list should not be ingested at any concentration. Numerous systems, most notably the endocrine system, are extremely sensitive to very low levels of chemicals, in parts-per-billion or less. The damage may not be evident at the time of exposure but can have unpredictable delayed, life-long effects on individuals and/or their offspring. Effects of this nature would be much harder to identify than obvious impacts such as skin and eye irritation that occur immediately upon contact. Health impairments could remain hidden for decades and span generations. Specific outcomes could include reduced sperm production, infertility, hormone imbalances, and other sex-related disorders. Further compounding this concern is the potential for the shared toxic action of these contaminants, especially those affecting the same and/or multiple organ systems.

It was difficult to arrive at a "short list" of chemicals that would be informative for water quality monitoring because of the vast array of products constantly being developed, and the wide selection of chemicals used in those products. We can,

Table 2. Chemicals with CAS numbers that have 10 or more adverse health effects.

| Chemical | CAS # | Number of products |
|---|------------|--------------------|
| (2-BE) Ethylene glycol monobutyl ether | 111-76-2 | 22 |
| 2,2',2''-Nitrilotriethanol | 102-71-6 | 3 |
| 2-Ethylhexanol | 104-76-7 | 7 |
| 5-Chloro-2-methyl-4-isothiazolin-3-one | 26172-55-4 | 2 |
| Acetic acid | 1186-52-3 | 1 |
| Acrolein | 107-02-8 | 1 |
| Acrylamide (2-propenamide) | 79-06-1 | 6 |
| Acrylic acid | 79-10-7 | 2 |
| Ammonia | 7664-41-7 | 3 |
| Ammonium chloride | 12125-02-9 | 2 |
| Ammonium nitrate | 6484-52-2 | 2 |
| Aniline | 62-53-3 | 1 |
| Benzyl chloride | 100-44-7 | 2 |
| Boric acid | 10043-35-3 | 4 |
| Cadmium | 7440-43-9 | 1 |
| Calcium hypochlorite | 7778-54-3 | 1 |
| Chlorine | 7782-50-5 | 1 |
| Chlorine dioxide | 10049-04-4 | 2 |
| Dibromoacetonitrile | 3252-43-5 | 1 |
| Diesel 2 | 68476-34-6 | 19 |
| Diethanolamine | 111-42-2 | 4 |
| Diethylenetriamine | 111-40-0 | 1 |
| Dimethyl formamide | 68-12-2 | 1 |
| Epidian | 25068-38-6 | 1 |
| Ethanol | 64-17-5 | 8 |
| Ethyl mercaptan | 75-08-1 | 1 |
| Ethylbenzene | 100-41-4 | 7 |
| Ethylene glycol | 107-21-1 | 17 |
| Ethylene oxide | 75-21-8 | 2 |
| Ferrous sulfate | 7720-78-7 | 1 |
| Formaldehyde | 50-00-0 | 4 |
| Formic acid | 64-18-6 | 8 |
| Fuel oil #2 | 68476-30-2 | 9 |
| Glutaraldehyde | 111-30-8 | 11 |
| Glyoxal | 107-22-2 | 2 |
| Hydrodesulfurized kerosene | 64742-81-0 | 1 |
| Hydrogen sulfide | 7783-06-4 | 1 |
| Iron | 7439-89-6 | 3 |
| Isobutyl alcohol (2-methyl-1-propanol) | 78-83-1 | 3 |
| Isopropanol (propan-2-ol) | 67-63-0 | 47 |
| Kerosene | 8008-20-6 | 3 |
| Light naphthenic distillates, hydrotreated | 64742-53-6 | 2 |

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Table 2. Chemicals with CAS numbers that have 10 or more adverse health effects. (*Continued*)

| Chemical | CAS # | Number of products |
|---|------------|--------------------|
| Mercaptoacetic acid | 68-11-1 | 2 |
| Methanol | 67-56-1 | 74 |
| Methylene bis(thiocyanate) | 6317-18-6 | 2 |
| Monoethanolamine | 141-43-5 | 5 |
| NaHCO ₃ | 144-55-8 | 5 |
| Naphtha, petroleum medium aliphatic | 64742-88-7 | 2 |
| Naphthalene | 91-20-3 | 18 |
| Natural gas condensates | 68919-39-1 | 1 |
| Nickel sulfate | 7786-81-4 | 1 |
| Paraformaldehyde | 30525-89-4 | 2 |
| Petroleum distillate/naphtha | 8002-05-9 | 7 |
| Petroleum distillate/naphtha | 8030-30-6 | 1 |
| Phosphonium, tetrakis(hydroxymethyl)-sulfate | 55566-30-8 | 2 |
| Propane-1,2-diol | 57-55-6 | 6 |
| Sodium bromate | 7789-38-0 | 1 |
| Sodium chlorite (chlorous acid, sodium salt) | 7758-19-2 | 1 |
| Sodium hypochlorite | 7681-52-9 | 1 |
| Sodium nitrate | 7631-99-4 | 3 |
| Sodium nitrite | 7632-00-0 | 3 |
| Sodium sulfite | 7757-83-7 | 1 |
| Styrene | 100-42-5 | 1 |
| Sulfur dioxide | 7446-09-5 | 1 |
| Sulfuric acid | 7664-93-9 | 1 |
| Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione (Dazomet) | 533-74-4 | 3 |
| Titanium dioxide | 13463-67-7 | 2 |
| Tributyl phosphate | 126-73-8 | 1 |
| Triethylene glycol | 112-27-6 | 1 |
| Urea | 57-13-6 | 3 |
| Xylene | 1330-20-7 | 11 |

however, provide some guidance by pointing out four types of chemicals that are used in a relatively high number of products. These include (1) the silicas, which appear frequently as product components; (2) potassium based chemicals, which are also found in numerous products, although with relatively low toxicity; (3) petroleum derived products, which take on many different forms (including some without CAS numbers), and some of which are toxic at low concentrations and might be detected with diesel or gasoline range organics tests; and (4) the alcohols for which new detection technology is being developed, and because they are among the chemicals with the most health effects.

Table 3. Chemicals with CAS numbers found in the highest number of products.

| Chemical | CAS # | Number of products | Number of health effects |
|---|------------|--------------------|--------------------------|
| Crystalline silica, quartz | 14808-60-7 | 125 | 7 |
| Methanol | 67-56-1 | 74 | 11 |
| Isopropanol (propan-2-ol) | 67-63-0 | 47 | 10 |
| Petroleum distillate hydrotreated light | 64742-47-8 | 26 | 6 |
| (2-BE) Ethylene glycol monobutyl ether | 111-76-2 | 22 | 11 |
| Bentonite | 1302-78-9 | 20 | 6 |
| Diesel 2 | 68476-34-6 | 19 | 10 |
| Naphthalene | 91-20-3 | 18 | 12 |
| Aluminum oxide | 1344-28-1 | 17 | 3 |
| Ethylene glycol | 107-21-1 | 17 | 10 |
| Sodium hydroxide | 1310-73-2 | 17 | 5 |
| Barite (BaSO ₄) | 7727-43-7 | 15 | 5 |
| Heavy aromatic petroleum naphtha | 64742-94-5 | 15 | 5 |
| Crystalline silica, cristobalite | 14464-46-1 | 14 | 5 |
| Mica | 12001-26-2 | 14 | 3 |
| Sodium chloride | 7647-14-5 | 14 | 9 |
| Crystalline silica, tridymite | 15468-32-3 | 13 | 3 |
| Hydrochloric acid (HCl) | 7647-01-0 | 13 | 7 |
| Glutaraldehyde | 111-30-8 | 11 | 11 |
| Xylene | 1330-20-7 | 11 | 10 |
| Guar gum | 9000-30-0 | 10 | 3 |
| Iron oxide (ferric oxide) | 1309-37-1 | 10 | 5 |
| 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 | 2 |
| Polyacrylamide/polyacrylate copolymer | 25085-02-3 | 9 | 3 |
| Sodium carboxymethylcellulose (polyanionic cellulose) | 9004-32-4 | 9 | 5 |
| Calcium hydroxide | 1305-62-0 | 8 | 8 |
| Crystalline silica (silicon dioxide) | 7631-86-9 | 8 | 4 |
| Ethanol | 64-17-5 | 8 | 12 |

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Table 3. Chemicals with CAS numbers found in the highest number of products.
(Continued)

| Chemical | CAS # | Number of products | Number of health effects |
|--|------------|--------------------|--------------------------|
| 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 |
| Asphaltite (gilsonite, hydrocarbon black solid) | 12002-43-6 | 7 | 4 |
| Butanol (n-butyl alcohol, butan-1-ol, 1-butanol) | 71-36-3 | 7 | 8 |
| Calcium carbonate (sized) | 471-34-1 | 7 | 6 |
| Calcium chloride | 10043-52-4 | 7 | 8 |
| Ethoxylated nonylphenol | 9016-45-9 | 7 | 6 |
| Ethylbenzene | 100-41-4 | 7 | 11 |
| Petroleum distillate naphtha | 8002-05-9 | 7 | 12 |
| Propargyl alcohol (prop-2-yn-1-ol) | 107-19-7 | 7 | 9 |
| Tetramethylammonium chloride | 75-57-0 | 7 | 8 |

Detection of increasing or elevated concentrations of these chemicals near gas operations could indicate that communication between natural gas activities and a water resource such as a domestic well, creek, pond, wetland, and so on is occurring. If a longitudinal monitoring program were to reveal any increase in concentration in one of these target groups, even if the concentrations were well below any water quality standards, it should trigger more testing immediately.

For many years, drillers have insisted that they do not use toxic chemicals to drill for gas, only guar gum, mud, and sand. While much attention is being given to chemicals used during fracking, our findings indicate that drilling chemicals can be equally, if not more dangerous. What we have learned about the chemicals used in the Crosby well blowout provides insight into why citizens living nearby suffered severe respiratory distress, nausea, and vomiting and had to be evacuated from their homes for several days. It might also shed light on why other individuals living near gas operations have experienced similar symptoms during the gas drilling phase (prior to fracking).

From the first day the drill bit is inserted into the ground until the well is completed, toxic materials are introduced into the borehole and returned to the surface along with produced water and other extraction liquids. In the western United States it has been common practice to hold these liquids in open evaporation pits until the wells are shut down, which could be up to 25 years. These pits have rarely been examined to ascertain their chemical contents outside of some limited parameters (primarily metals, chlorides, and radioactive materials). Our data reveal

that extremely toxic chemicals are found in evaporation pits and indeed, these and other similar sites may need to be designated for Superfund cleanup. In the eastern United States, and increasingly in the West, these chemicals are being re-injected underground, creating yet another potential source of extremely toxic chemical contamination. In other words, what ends up in evaporation pits in the West will in other parts of the country be injected underground.

RECOMMENDATIONS

TEDX has collected the names of nearly a thousand products used in natural gas operations in the United States. We have no idea how many more products are in use. We have health data on only a small percentage of the chemicals in use because CAS numbers are often not provided on MSDSs and without a CAS number it is difficult to search for health data. Working under the assumption that our results underestimate the consequences of the health impacts to the labor force, residents living in close proximity to the wells, and those dependent upon potable and agricultural water that could be affected by natural gas operations, we make the following recommendations:

1. Product labels and/or MSDSs must list the complete formulation of each product, including the precise name and CAS number and amount of every chemical, as well as the composition of the vehicle used to fill the product container. To prevent serious injury and mortality the products used during natural gas operations should be exempt from confidentiality.
2. If an ingredient does not have a CAS number it must be clearly defined, leaving no doubt about its possible health impact(s).
3. Records should be kept for each drilling and fracking operation, listing the total volume of fluid injected, the amount of each product used, the depth at which the products were introduced, and the volume of fluid recovered.
4. The volume and concentration of all liquids and solids removed from the work sites should be made available to the public. Without this information the full health and environmental hazards posed by natural gas production cannot be predicted.
5. Air quality monitoring for individual VOCs as well as ozone must become standard procedure in any region where natural gas activity is taking place and must commence prior to initiation of operations to establish baseline levels. Estimating tonnage of VOCs and NO_x released and ignoring ozone should no longer be the practice.
6. Comprehensive water monitoring programs should be established in every gas play across the United States both prior to and after gas production commences, that include new chemical species indicators based on toxicity and mobility in the environment, to monitor sub-surface and above-surface domestic and agricultural water resources, and all domestically used aquifers and underground sources of drinking water.
7. We recommend the development of labeled isotopic fingerprints of the chlorinated compounds in products used to drill and fracture. Each manufacturer

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would have its own fingerprint. A plot of this isotopic data found down gradient of a hydraulically fractured well would aid a state or federal regulator in identifying the contamination source.

8. Given the general consistency of reported adverse health effects by citizens and laborers across many gas plays, public health authorities should establish an epidemiological monitoring program that merges at the state and national level in order to increase power and be able to reach conclusions early on. The design of the study should include environmental monitoring of air and water as well as any health changes in those living and working in regions of natural gas operations. The health monitoring should be able to detect early trends in parameters, such as asthma, hypertension, chemical sensitization, chronic skin and eye irritation, and neurological alterations, to mention a few.
9. As underground injection of waste is becoming the most frequent choice for waste disposal, rigid accounting of the date, volume, and source of all materials, and the exact location in the geological formation(s) in which it is injected should be become a part of permanent government records that will be publicly available for future generations.
10. Before a permit is issued to drill for natural gas, complete waste management plans should be reviewed and approved and become part of the permit.
11. The injection of hydraulic fracturing fluids should be regulated under the Safe Drinking Water Act. This is needed to assure mechanical integrity of the injection wells and isolation of the injection zone from underground sources of drinking water.

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