**Supporting Information: Overview of Chronic Oral Toxicity Values for Chemicals Present in Hydraulic Fracturing Fluids, Flowback and Produced Waters**

Erin E. Yost[1‡], John Stanek[2], Robert S. DeWoskin[2§], Lyle D. Burgoon*[2†]

[1] Oak Ridge Institute for Science and Education (ORISE) Research Participation Program at the United States Environmental Protection Agency, National Center for Environmental Assessment, Research Triangle Park, NC

[2] United States Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Research Triangle Park, NC

‡ Present address: United States Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Research Triangle Park, NC

§ Present address: etioLogic, LLC, Durham, NC 27712

† Present address: Environmental Laboratory, US Army Engineer Research and Development Center, Research Triangle Park, NC

*Indicates corresponding author

**TABLE OF CONTENTS:**

**Table SI-1. Description of sources used by EPA to create lists of chemicals used in hydraulic fracturing fluids or detected in flowback or produced water.**

[a] Sources used to identify chemicals used in hydraulic fracturing fluids.
[b] Sources used to identify chemicals detected in flowback and produced water.

| Description / Content | Reference |
|---|---|
| Chemicals and other components used by 14 hydraulic fracturing service companies from 2005 to 2009 as reported to the House Committee on Energy and Commerce. For each hydraulic fracturing product reported, companies also provided an MSDS with information about the product's chemical components. | US House of Representatives (2011)[1][a] |
| Chemicals used during natural gas operations with some potential health effects. The list of chemicals was compiled from MSDSs from several sources, including the Bureau of Land Management, U.S. Forest Service, state agencies, and industry. | Colborn et al. (2011)[2][a] |
| Chemicals used or proposed for use in hydraulic fracturing in the Marcellus Shale in New York based on product composition disclosures and MSDSs submitted to the New York State Department of Environmental Conservation (NYSDEC). Also includes data provided separately to NYSDEC by well operators on analytical results of flowback water samples from Marcellus Shale operations in Pennsylvania and West Virginia. | New York State Department of Environmental Conservation (2011)[3][a,b] |
| Chemicals reported to be used by nine hydraulic fracturing service companies from 2005 to 2010. Companies provided the chemical names in MSDSs, product bulletins, and formulation sheets. | US EPA (2013)[4][a] |
| MSDSs provided to the EPA during on-site visits to hydraulically fractured oil and gas wells in Oklahoma and Denver. | Material Safety Data Sheets[5][a] |
| Characteristics of undiluted chemicals found in hydraulic fracturing fluids associated with coalbed methane production, based on MSDSs, literature searches, reviews of relevant MSDSs provided by service companies, and discussions with field engineers, service company chemists, and state and federal employees. | US EPA (2004)[6][a] |
| Chemicals used in Pennsylvania for hydraulic fracturing activities based on MSDSs provided by industry. | Pennsylvania Department of Environmental Protection (2010)[7][a] |
| Chemical records entered in FracFocus by oil and gas operators for individual wells from January 1, 2011, through February 28, 2013. FracFocus is a publicly accessible hydraulic fracturing chemical registry developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. Chemicals claimed as confidential business information (CBI) do not have to be reported in FracFocus. | US EPA (2015)[8][a] |
| Chemicals detected in flowback from 19 hydraulically fractured shale gas wells in Pennsylvania and West Virginia, based on analyses conducted by 17 Marcellus Shale Coalition member companies. | Hayes (2009)[9][b] |
| Chemicals reportedly detected in flowback and produced water from 81 wells provided to the EPA by nine well operating companies. | US EPA (2011)[10][b] |

**Table SI-2:** Sources used by EPA to identify toxicity values

| Source | Website |
|---|---|
| EPA Integrated Risk Information System (IRIS) database | http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList |
| EPA Human Health Benchmarks for Pesticides (HHBP) database | http://iaspub.epa.gov/apex/pesticides/f?p=HHBP:home |
| EPA Provisional Peer-Reviewed Toxicity Value (PPRTV) database | http://hhpprtv.ornl.gov/index.html |
| Agency for Toxic Substances and Disease Registry (ATSDR) Minimum Risk Levels | http://www.atsdr.cdc.gov/toxprofiles/index.asp#bookmark05 |
| California Environmental Protection Agency (CalEPA) Toxicity Criteria Database | http://oehha.ca.gov/tcdb/index.asp |
| World Health Organization (WHO) International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD) | http://www.who.int/ipcs/publications/cicad/en/ |

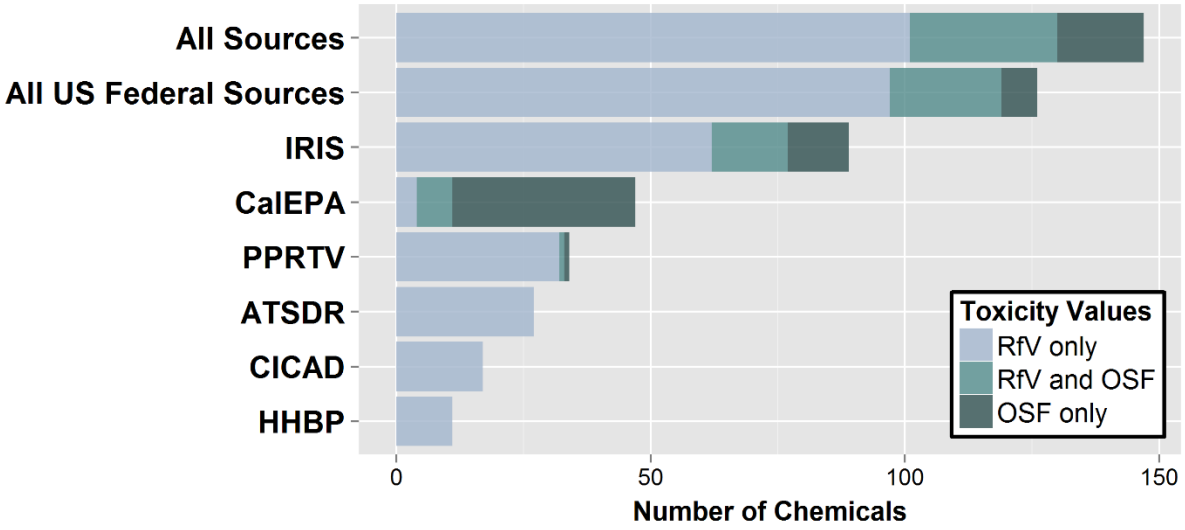


**Figure SI-1:** Number of chemicals with chronic oral RfVs or OSFs, showing the contribution from each data source. "All Sources" refers to the composited values available from all six sources listed in Table SI-2. "All US Federal Sources" refers to the composited values available from IRIS, PPRTV, ATSDR, and HHBP.

**Background: EPA's FracFocus 1.0 project database**

The project database from EPA's *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0* is a Microsoft Access database requiring Microsoft Access 2007 or later. The database was created to support analyses of FracFocus 1.0 disclosures (the operator-submitted information to the FracFocus Registry of water and chemical use in hydraulically fractured wells). In addition to containing the data representing water and chemical use by operators of hydraulically fractured wells, the database also contains the tables and queries used to generate tables, figures, and in-text numbers that were used throughout EPA's *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0* and parts of EPA's draft *Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources*. The database is available in a zip file on EPA's website: http://www3.epa.gov/research/FracFocus/EPAFracFocusData.zip. The database file is named "FracFocus_03-2015.accdb."

When working in the Access database, users can double-click a table or query listed in the navigation pane on the left to view the contents of the table or query (if the navigation pane is hidden, click the arrows at the top to expand it, or press F11 to show it again). In addition, users can write their own custom queries of the tables and queries within the database. Finally, users can also write code in R (or another language) to interface with the database to design and generate other specific analyses. The specific query used in this study is described in detail below.

**Query used to determine frequency of chemical use from EPA's FracFocus 1.0 project database:**

In order to determine the frequency of use for all unique chemicals identified by EPA's *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0*, two queries were run on the "QaIngredient" tab of the Access database:

1. The first query selects all chemical ingredient records from deduplicated disclosures within the study time period and with a valid CASRN, and groups them by CASRN. The query returns the total number of well disclosures and total number of ingredient records that were associated with each chemical:

```
SELECT ChemicalName, Cas, count(*) AS Disclosures, sum(SQ.Ingredients) AS Ingredients FROm
(SELECT QaWell.WellID, ChemicalName, Cas, count(*) AS Ingredients
FROM QaWell INNER JOIN QaIngredient ON QaWell.WellId = QaIngredient.WellId
WHERE Authoritative=Yes AND left(dateffflag,2)='OK' AND ValidCas=Yes
GROUP BY QaWell.WellID, ChemicalName, Cas) AS SQ
GROUP BY ChemicalName, Cas
ORDER BY count(*) DESC, ChemicalName ASC
;
```

2. A second query was then run on the "QaIngredient" tab of the Access database, in order to determine the total number of well disclosures and ingredient records in the database. This query selects all ingredient records from deduplicated disclosures within the study time period and with a valid CASRN, just like above, and summarizes the entire set of records on a single row:

```
SELECT count(*) AS Disclosures, sum(SQ.Ingredients) AS Ingredients FROm
(SELECT QaWell.WellID, count(*) AS Ingredients
FROM QaWell INNER JOIN QaIngredient ON QaWell.WellId = QaIngredient.WellId
WHERE Authoritative=Yes AND left(dateffflag,2)='OK' AND ValidCas=Yes
GROUP BY QaWell.WellID) AS SQ
ORDER BY count(*) DESC
;
```

Results of these queries were then copied into a Microsoft Excel file. Frequency of use was calculated as the ratio of the number of disclosures for each individual chemical (from the first query), divided by the total number of disclosures on the database (from the second query). As used in this report, "disclosure" refers to all data submitted for a specific oil or gas production well for a specific fracture date.

The project database was accessed on June 15, 2015.

**REFERENCES FOR SUPPORTING INFORMATION:**


1. *Chemicals used in hydraulic fracturing*. U.S. House of Representatives, Committee on Energy and Commerce, Minority Staff: Washington, D.C., 2011.

2. Colborn, T.; Kwiatkowski, C.; Schultz, K.; Bachran, M. Natural Gas Operations from a Public Health Perspective. *Hum. Ecol. Risk Assess.* **2011**, 17, (5), 1039-1056.

3. *Revised draft supplemental generic environmental impact statement (SGEIS) on the oil, gas and solution mining regulatory program: Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus shale and other low-permeability gas reservoirs*; New York State Department of Environmental Conservation (NYSDEC): Albany, NY, 2011. http://www.dec.ny.gov/energy/75370.html.

4. *Data received from oil and gas exploration and production companies, including hydraulic fracturing service companies 2011 to 2013. Non-confidential business information source documents are located in Federal Docket ID: EPA-HQ-ORD2010-0674;* http://www.regulations.gov/#!docketDetail;rpp=100;so=DESC;sb=docId;po=0;D=EPA-HQ-ORD-2010-0674.

5. Material Safety Data Sheets. (a) Encana/Halliburton Energy Services, Inc.: Duncan, Oklahoma. Provided by Halliburton Energy Services during an onsite visit by the EPA on May 10, 2010; (b) Encana Oil and Gas (USA), Inc.: Denver, Colorado. Provided to US EPA Region 8.

6. *Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs*; EPA/816/R-04/003; U.S. Environmental Protection Agency, Office of Solid Waste: Washington, D.C., 2004.

7. *Chemicals used by hydraulic fracturing companies in Pennsylvania for surface and hydraulic fracturing activities*. Pennsylvania Department of Environmental Protection (PADEP): Harrisburg, PA, 2010. http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/Frac%20list%206-30-2010.pdf.

8. *Analysis of hydraulic fracturing fluid data from the FracFocus chemical disclosure registry 1.0: Project database*; EPA/601/R-14/003; Office of Research and Development, U.S. Environmental Protection Agency: Washington, D.C., 2015. http://www2.epa.gov/hfstudy/epa-project-database-developed-fracfocus-1-disclosures.

9. Hayes, T., *Sampling and analysis of water streams associated with the development of Marcellus shale gas*; Marcellus Shale Coalition: Des Plaines, IL, 2009. http://eidmarcellus.org/wp-content/uploads/2012/11/MSCommission-Report.pdf.

10. *Sampling data for flowback and produced water provided to EPA by nine oil and gas well operators (non-confidential business information);* http://www.regulations.gov/#!docketDetail;rpp=100;so=DESC;sb=docId;po=0;D=EPA-HQ-ORD-2010-0674.