Human Toxicity Impact of Shale Gas and Coal

by

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Abstract

Rapid increases in production of shale gas via high volume hydraulic fracturing has resulted in a variety of environmental concerns. One of the most controversial elements of shale gas production is the lack of data regarding potential water contamination and human toxicity. This study analyzes the relative human toxicity impact of electricity produced from shale gas and coal. Using a life cycle approach, the human toxicity impact (HTI) of electricity produced from shale gas is an order of magnitude lower than electricity produced from coal, even when toxic emissions from coal mining operations are not included. Air emissions of mercury are the largest contributor to the human toxicity impact of coal electricity, whereas barium contained in produced water from hydraulic fracturing operations is the largest contributor for the HTI of electricity from shale gas. A scenario analysis indicates that the HTI of shale gas could approach the HTI of coal if containment failures occur that lead to the discharge of untreated flowback water into surface water; however, when analogous containment failures of the coal system are taken into account, the HTI of coal electricity is 2-3 orders of magnitude greater than electricity produced from shale gas. The results of the analysis can be used to identify areas for improvement and calculate relative toxicity between the two systems. Given the lack of exposure data and large inherent uncertainty in toxicity factors, the results cannot be used to infer absolute human health impacts from either system.

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Contents

Introduction

The electricity sector in the United States is made up of 39% coal and 27% natural gas. (*1*) The proportion of natural gas produced via high volume hydraulic fracturing, or fracking, has increased rapidly. Shale gas represented 5% of natural gas production in 2005 and 47% of natural gas production in 2014. While some regions of the United States have embraced hydraulic fracturing operations due to economic benefits, others have enacted moratoria or outright bans on hydraulic fracturing due to environmental concerns. (*2*) Scientific understanding of the environmental impacts of fracking has not kept pace with the rate of industrial development. (*3*) One of the largest environmental concerns surrounding hydraulic fracturing (HF) operations is the potential impact to drinking water; however, there is a great deal of uncertainty regarding both the actual sources of contamination and the extent to which drinking water quality is impacted. (*4, 5*)

Relatively few studies have addressed the water contamination and human health concerns of hydraulic fracturing. The US Environmental Protection Agency recently released a draft assessment of potential drinking water impacts associated with shale gas, and several other studies have quantified the changes in water quality due to introduction of a hydraulic fracturing operation. (*6*) None of these studies contextualize the potential human health impacts of shale gas relative to other sources of electricity. Continued penetration of shale gas into the power sector will displace other sources of electricity, such as coal and conventional natural gas. It is reasonable to assume that shale gas will cause greater environmental damage than conventional natural gas and renewable energy technologies (*7*); however, the tradeoffs between shale gas and coal are less clear.

Comparative life cycle assessments for shale gas and coal have shown that the greenhouse gas emissions (GHG) associated with electricity produced from shale gas appear to be lower than electricity produced from coal, with estimates ranging from 450-488 kg CO2-e/MWh for shale gas as opposed to 900 kg CO2-e/MWh for coal. (*8*) (*9*) (*10*) However, Howarth et al. showed that the greenhouse gas footprint (grams carbon per MJ) of shale gas is larger than coal. (*11, 12*) Estimated water intensity of shale gas varies among different studies, however, they have the same conclusion that the water usage during HF and well operation is less than the water used for coal washing and cooling in coal power plants. (*13, 14*) Kondash and Vengosh also claimed that HF is not extracting more water relative to conventional oil or coal mining when normalized to the energy production. (*15*)

Although the number of life cycle assessment (LCA) studies have increased, most are focused on GHG emissions, water use, and criteria air emissions. (*8, 15-17*) There is a literature gap comparing the human toxicity impact of shale gas and coal. Although chemical spills on HF sites, acid mine drainage contaminations, and other pollutants from shale gas and coal have been reported by several studies (*18, 19*), data are fragmented and analyses are often confined to a limited number of individual pollutants. There are numerous difficulties associated with making a comparison between shale gas and coal, as the human toxicity concerns associated with electricity produced from different resources are quite different,. Jiang et al. assessed different scenarios of HF wastewater disposal by TRACI (a tool for reduction and assessment of chemical and other environmental impacts) (*20*). The result shows eutrophication potential, freshwater ecotoxicity potential, carcinogenic potential and noncarcinogenic potential, however, this analysis in isolation is not useful to compare the impacts of HF with other energy sources. While one LCA study has attempted to calculate human toxicity impact as part of a suite of metrics to compare electricity produced from shale gas, coal, nuclear, and PV (*21*) , the analysis has been criticized for inconsistent boundaries and unreasonable disposal scenarios. (*22*) This research calculates the HTI to compare potential human toxicity impacts of electricity produced from shale gas and coal in detail.

The HF process includes injection of high-pressure fluids designed to fracture the reservoir and promote economic natural gas production from low permeability shale. Fracking fluids are primarily water, but also contain additives such as quartz sand proppant, biocide, acid, and surfactants. These additives may serve to enhance fracture generation, help maintain fracture permeability, and reduce down hole fouling, all of which improve shale gas extraction efficiency. After HF well completion, a majority of the injected water returns to the surface and is referred to as ‘flowback’ water. Proper management of flowback wastewaters is crucial to preventing environmental contamination, as flowback is often highly saline and contains elevated levels of barium and naturally occurring radioactive material. Shale gas wells will also produce brine from the shale reservoir throughout the well production lifetime. Collectively, flowback and produced brine are the largest volume waste stream associated with shale gas production. (*23*) The most common disposal method for these waste fluids is deep well injection in EPA permitted class II brine injection wells (*24*). When deep well injection is not feasible or is less economical, produced fluids may be reused to frack additional wells. This practice has become more common in areas where water scarcity is a concern or where brine disposal wells are not abundant. (*25*) Improper disposal of flowback and produced brines has led to contamination of fresh water resources in several instances, such as radioactive contaminants and bromine contamination for drinking water. (*26, 27*) Data collected at a Pennsylvania Wastewater Treatment Plant (WWPT) (*27*) shows that the effluent increased downstream concentration of chloride and bromide above background level. Though radium was reduced by more than 90% of the influent concentraion, it was still above radioactive waste disposal threshold regulation whose impact can’t be ignored. Ferrar et al. (*28*) gives similar result. Pennsylvania Department of Environmental Protection requested drilling companies stop disposing their wastewater through WWTPs in 2011. Besides potential pollutants, spills and storage failures are other current environmental concerns for HF. EPA just published a draft and explicit a whole chapter for those accidents. (*6*)

Contamination from coal mining and coal-fired power plants has been examined for decades. (*19, 29-31*) After mining, heavy metals and low pH in acid mine drainage might flow out after participate and damage the aqua life and pollute the drinking water source. However, it is hard to quantify how much acid mine drainage is produced by a mining site and who should be responsible for the contamination, because baseline data is not available before coal mining activity at Pennsylvania in late 1700s (*30*). Compared with coal mining activity, it is easier to track pollutants in coal power plants, including mercury emissions, NO_x and SO_2, and particulate matters emissions. Although some of the combustion residuals are captured from air emission to soil waste, the impoundment system still have water effluent that might have negative environmental impact. (*32*) Several organizations and researchers assessed the impact of coal power plants. Korre et al. pointed out that the human toxicity impact within coal power plants: a 500 MW capacity PC Wall-fired dry bottom boiler coal power plant has 8845 kg 1,4-DB eq human toxicity impact. (*33*) Babbitt and Lindner showed total human toxicity impact for baseline coal combustion products (100% disposal coal combustion products in landfill 50% and surface impoundment 50%) is 5.4e-4 to 4.6e-3 DALY per 1000 kg of coal combusted (*34*).

This study takes a life cycle approach to quantify the relative human toxicity index (HTI) of electricity produced from shale gas and coal. HTI quantifies the inherent toxicity burden associated with emissions from a product or process and is a commonly used within LCA. The product or process might involve several chemicals associated with emissions. To build the toxics release inventory, each chemical emitted to the environment is weighted by human toxicity potential (HTP) of unit chemical. (*35*) An aggregated score for all chemicals is called HTI, and usually for comparing purpose, HTI will be normalized by functional unit. An HTI calculation makes generic assumptions regarding fate and exposure that are applied consistently across all systems to serve as a screening tool that can be used to inform more comprehensive risk assessments. (*35*) The implications of using the HTI method in the context of the results is discussed in detail.

Methods

Boundary and Scope

This study assesses the human toxicity impact of electricity produced from shale gas and coal. Only emissions that affect human toxicity are included in the analysis. Engineering processes sketch and pollutant emissions' relative magnitudes are shown in Figure 1 a) and b). Boundaries for LCA of these two energy sources are shown in Figure 1 c) and Figure 1 d). For shale gas, emissions from the hydraulic fracturing process and electricity generation are assessed, including air emissions of NO_x and SO_2, as well as aquatic emissions from chemical inputs to fracturing fluid and the constituents of flowback and produced water. For coal, emissions from electricity generation and wastewater impoundment are analyzed, including air emissions of NO_x, SO_x, and mercury, as well as aquatic emissions from combustion residuals. Acid mine drainage from coal mining is not included in this study due to data limitations. Toxicity associated with infrastructure, transportation and cooling water are not included in the life cycle for either energy source, because they have minor contribution to the whole process (*20, 29*). Also, particulate matter (PM) is not included due to unknown characterization factors (CF) in USEtox and ReCiPe (refer to Section 2.3). Because of the data limitations surrounding acid mine drainage and PM, it is expected that toxic emissions from coal are underestimated by this study.

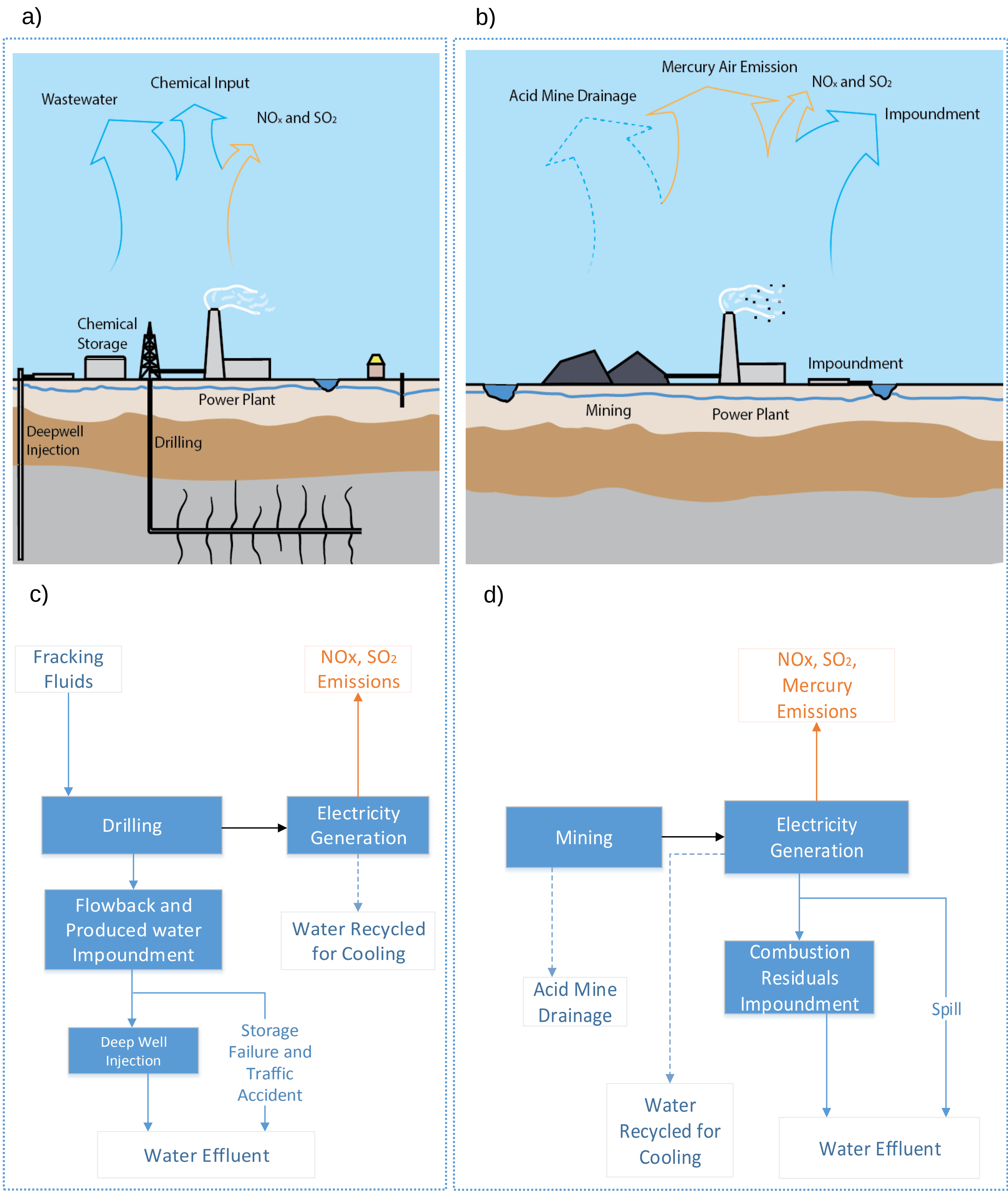

Figure 1 a) Sketch of engineering process for shale gas, including HF and gas combustion in a power plant; b) Sketch of engineering process for coal, including coal mining and coal combustion in a power plant; c) Flow diagram and emissions source of shale gas; d) Flow diagram and emissions source of coal. Blue solid boxes represent unit processes, transparent boxes stand for final emission, and unboxed text means operational condition. Dot lines mean those pollutants existing in the life cycle but excluded in this study. Orange solid line and text mean air emissions and blue solid line and text mean water emissions

Emissions data was obtained from 2010-2015. Whenever possible, data from Pennsylvania was used, given the predominance of both shale gas and coal within the region. The Marcellus Region, mostly located in West Virginia and Pennsylvania, produced the largest volume of shale gas in the United States in 2014, accounting for almost 40% of total U.S. shale gas production. (*1*) Coal production in Appalachian coal basin decreased from almost 50% in 1985 to 27% in 2011. (*36*) Historically, Appalachian coal basin used to be the biggest coal production area. National averages were used whenever state-level data was unavailable.

Scenarios Evaluated

This study evaluates a baseline case for electricity produced from both shale gas and coal, as well as scenarios that include unintentional releases of waste for each system. Unintentional release of flowback water to surface water has been identified as one of the major sources of water contamination from hydraulic fracturing. (*23*) In order to capture the risks of casing failures and accidental releases, scenarios that include failure events are integrated into the analysis and are shown as alternate emission pathways in Figure 1 c). In total, 3 different scenario comparisons for environmental emissions are considered: (1) Baseline-case for shale gas and baseline-case for coal; (2) worst-case for shale gas and baseline-case for coal; (3) worst-case for shale gas and worst-case for coal.

The baseline case for electricity produced from shale gas assumes steam electricity generation. (*37*) A conservative pollutant emissions are assigned to shale gas: chemicals in fracking fluids are accidentally released in the surface water and 1% of produced water (flowback water and produced brine) is spilled in the surface water as well. It also assumes adequate treatment and deep well injection of produced water. Thus, in this study the baseline-case for shale gas is overestimate the emissions compared with business-as-usual case (BAU). Ideally, LCA evaluates BAU of a product or a process for current management purpose, however, data is not abundant nor precise enough for rigorous analysis. For chemical use in HF, there is no current integrated database that records spill rate, spill volume, location (*38*), which makes BAU evaluation impossible. For the worst case scenario for shale gas, 100% of all fracking chemicals and produced water are released into surface water.

The baseline case for electricity produced from coal does not specify the type of electricity generation because it is associated with the emissions for each power plant. All emissions, including air emission from power plant and unintentional water effluent from impoundment, confirm to the regulation. Pollutant emissions from mining site, such as acid mine drainage, are not captured in this study. The worst-case for coal includes unintentional release of coal ash into surface water, similar to impoundment failures that occurred in Kingston, TN in 2008. While significantly less frequent or likely than casing failures or produced water impoundment failures, coal ash spills are much larger in scope. Detailed emission data and electricity generation data are provided in supporting information (Table S3).

Human Toxicity Calculations

To calculate the human toxicity impact (HTI) of the two energy systems, the USEtox 2.0 (released in 2015) and ReCiPe 1.1 (released in 2014) databases are used. (*39, 40*) These two databases provide CFs that estimate human health and ecosystem damage for a wide range of chemicals. USEtox 2.0 is a scientific consensus model recommended as the preferred database for calculating HTI by the United Nations Environment Programme and the Society of Environmental Toxicology and Chemistry's Life Cycle Initiative. ReCiPe was developed by a consortium of LCA practitioners. The two databases were developed independently, and both provide endpoint level CFs for carcinogenic and non-carcinogenic toxicity, which translate dose effect to disability-adjusted life years (DALY). DALY is defined by World Health Organization as one lost year of "healthy" life due to disease and disability. In USEtox, healthy life is a standard reference life as 70 year, however, ReCiPe applies years of life lost and years of life disabled without age weighting and discounting, as a default setting for quantifying the damage contributing to the human health area of protection within LCA. (*40, 41*) ReCiPe and USEtox use different methods to obtain HTI factors and can produce results that can be very different. (*40*) Results from both databases are reported here due to the large degree of uncertainty in developing appropriate CFs and differences in CFs for key constituents of this analysis.

We compare and contrast these two characterization methods. Human toxicity indicators are selected for North America, and there is no specific category for each state. As this is not a risk assessment study, the toxicology of the chemicals is not provided.

Here we report toxic emission loads associated with electricity produced from shale gas and coal as DALY/GWh. Equation (1) is the generic form for calculating HTI. Modifications to Equation 1 given different forms of input data are included in the supporting information.

$$Human\ Toxicity\ Potential = \frac{Characterization\ Factor \times \frac{Mass\ emission}{mass\ fuel}}{\frac{GWh\ electricity\ produced}{mass\ fuel}} \qquad (1)$$

CF is given as DALY/kg emitted; the mass of chemicals per mass of fuel is in kg emission/kg fuel; the electricity generation is in GWh/mass fuel.

Data and Assumptions

Shale gas

Chemicals disclosure data was extracted in a machine-readable (SQL) format from FracFocus 3.0. (*42*) FracFocus is a database recording chemical use for HF from over 62,000 wells, and this study sampled to account for differences in chemical compositions due to geographic and operational variations by averaging well information for each Pennsylvania county represented in FracFocus as of December 2015. Over 2990 wells were surveyed, containing a total of 368 chemicals. The ID number, total well volume, chemicals contained in the formulation, purpose of each chemical (corrosion inhibitor, proppant, etc.), and the concentration of each component were recorded for each well. Not all wells use same chemicals, so we took top 100 most frequently used chemicals for Pennsylvania HF from 2010 to 2015 and assume those chemicals are used for each well. 38 of them have CF information in USEtox and 30 of them have CF in ReCiPe. Some chemical constituents are unknown due to proprietary claims by industry. Also, no further research shows whether those chemicals have severe environmental impact or not. Only those chemicals that have the potential to cause direct harm to humans or other organisms consumed by human are included due to the number of chemicals to be tracked.

To calculate productivity of the well as it changes over time, we use the Arps equation to estimate estimated ultimate recovery (EUR) for shale gas. (*43*) Arps Decline Curve Analysis has been the chosen method for evaluating estimated ultimate recovery (EUR) in oil and gas wells since the 1950's. Baseline productivity was assumed to be 4.26 Mmcf accumulated over 15 years production, (*44*) which is within the range of other research data (Table S3).

In addition to tracking the chemicals in the fracking fluid, the analysis includes chemicals contained in produced water that result from naturally dissolved materials. It is assumed that all fracking fluid chemicals are eventually returned via brine. To quantify the mass of chemicals in produced water, we make several assumptions about volume and concentration according to different studies. (*2, 20, 45*) The volume of flowback water is 15% of the injected water without recycling and the volume of produced brine is 5% of the injected water. There is no criteria defining flowback water and produced brine, but it is commonly assumed that the water collected at the surface within the first 14 days is considered flowback water, while water collected after 14 days is considered produced brine. (*46*)

The mechanism controlling the partitioning of naturally-occurring compounds from rocks to produced water is not well studied, yet it has been suggested that the majority of produced water constituents arise from mixing with native formation brines. (*23*) Data from Hayes (*46*) shows that the concentration of barium are 1.5 times greater in produced brine than flowback water. Concentrations of other naturally-occurring compounds either decrease or increase less than one and half times. Thus, we assume barium concentration in produced water is 1.5 times larger than flowback water and concentrations of other chemicals stay the same as flowback water. To include the most recent data, flowback water composition date is taken from Abualfaraj et al. (*45*) who compiled 35,000 data entries for Marcellus shale gas region. Some of the chemicals in produced water, especially organic compounds, are coming from the injected fracking fluids. However, there is no scientific evidence to confirm these constituents are from fracking fluids and some of them might react with each other to generate new chemical forms. Given this uncertainty, there is no way to differentiate naturally-occurring organic compounds from those that were injected, and thus, such chemicals may be double counted in the analysis. This again results in shale gas chemical emissions being overestimated in this study.

Current regulations for produced water prohibit treatment at WWTPs, so it could be either transported to centralized wastewater treatment plants or injected into geologic formations. Insufficient data exists to determine whether the injected chemicals remain stored within the disposal formation or migrate toward freshwater aquifers. Although deep well injection might not have toxic chemical released from the well, the traffic accidents and storage failure might happen. We estimate that the mass of barium after either treatment method is smaller than 1% of produced water. (*27, 47*)

<u>Coal</u>

For the baseline case for coal-fired electricity, reported air emissions from the TRI database where used. Coal ash was assumed to be disposed in wet-storage impoundments. To determine human toxicity of mercury emissions from coal-fired power plants, this study used data collected from the 100 largest power producers in the United Sates. (*48*) NO_x and SO_2 emission data was collected from the EPA Air Markets Program for coal power plants in Pennsylvania. (*49*) Although the coal ash is stored in regulated impoundments, some effluent is released to nearby surface water. To estimate water quality impacts of coal combustion residuals impoundment effluent, a University of North Carolina study was used. (*50*) We assume the coal ash impoundment factors to be representative of the industry as a whole. Once the spill happened, it would be hard to make a completely clean-up, because some of the combustion residuals are flushed to downstream where we hardly know the boundary. The worst case for coal in this study tracks the mass of original coal ash and take the soil ratio to calculate the mass of each element in the combustion residuals. The coal ash sedimentation on the river bed might continuously release hazardous heavy metals, such as mercury and arsenic. (*51, 52*) To be pointed out, the concentration of chemicals after the spill is usually published to the public, however, it is not very clear how big impact the spill remains because it is largely diluted by the river flow. Thus, using concentration and water flow is not a good way to assess the impact of the spill.

Sensitivity Analysis

A sensitivity analysis is conducted to compare the relative importance of parameters impacting predicted HTI. In this study, we change each of the data input either to its extreme values and remain the rest in average value to see the uncertainty of each parameter and how HTI is influenced by those changes. Data input is shown in Table SX.

Result

Three scenario evaluations compare the human toxicity impact of electricity produced from shale gas and coal. Figure 2.1 summarizes the three scenario comparisons: first, baseline-case for shale gas has lower HTI than coal; second, if the wastewater of HF is not treated at all, the worst-case for shale gas has a relatively similar HTI with baseline-case for coal; third, the worst-case for coal is larger than the worst-case for shale gas.

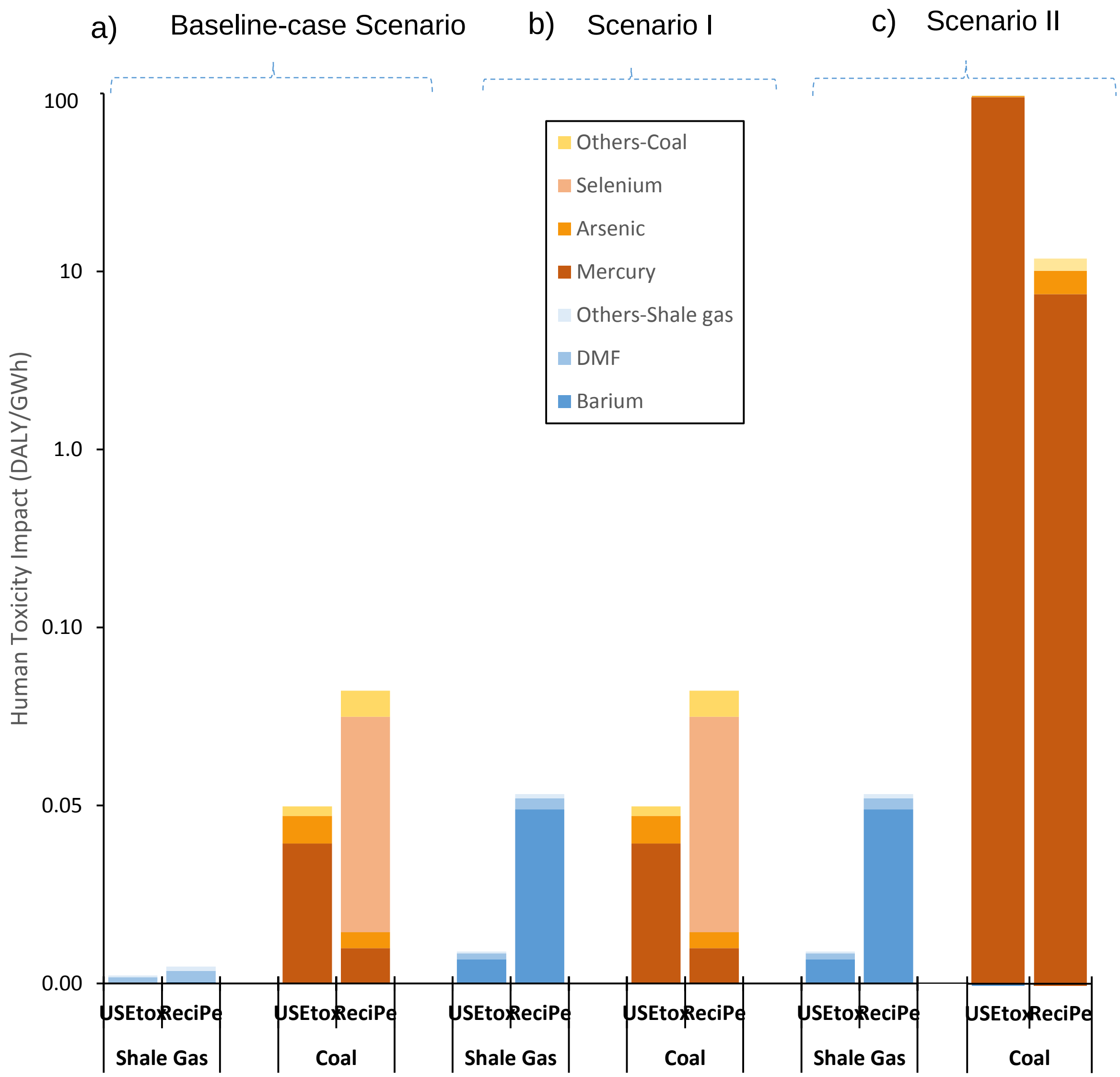

Figure 2.1 a) HTI of baseline-case scenario for shale gas and coal; b) HTI of scenario I: worst-case for shale gas and baseline-case for coal; c) HTI of scenario II: worst-case for both shale gas and coal. Figure 2.1 a), b), and c) share the same y-axis. Y-axis is not in a uniform scale.

Baseline-case Scenario

The baseline-case scenario likely underestimates the impact of coal while overestimating the impact of shale gas. This means that the HTI of BAU for shale gas is less than the baseline used here, and the HTI of BAU for coal is higher than the baseline used here. Figure 2.1 a) shows HTI of the baseline-case for coal-fired electricity is one order of magnitude larger than shale gas electricity when analyzed by either USEtox or ReCiPe. Thus, under BAU, HTI of shale gas will be more than one order of magnitude larger than coal. There are two main reasons for that. First, N,N'-Dimethylformamide (DMF) contributes most to the predicted HTI are chemical emissions, shown in Figure 2.1 a), and it is only used at the beginning of a HF operation. As the well is operated longer, the impact of fracking chemicals on the HTI is reduced, and chemicals associated with produced water becomes to the main factors. As shown in Figure S3, more shale gas generation will lead to less emission intensity. However, pollution from coal has a first order producing relationship with electricity generation, which means emission intensity for coal production is not affected by time. In Figure 2.1 a), DMF contribute the most to HTI of shale. Compared with mercury emitted from coal power plants, chemicals in fracking fluids have over eight orders of magnitude lower human toxicity CFs. Some of them are largely used in other industries, such as ethylene glycol, although they are not non-toxic to human. Dose-response information for those chemicals is provided in Table S4.

Scenario I

Scenario I compared the worse-case for shale gas and the baseline-case for coal to understand the HTI of all emissions from shale gas. Figure 2.1 b) shows that while the HTI of shale gas doubles, it is still one fifth of coal if USEtox method is applied on the model, however, ReCiPe method shows that the mean HTI value of shale gas is two third of coal. Although the HTI of shale gas is still smaller than coal by either methods, the difference between worst-case for shale gas and baseline-case for coal is not significant. The reason of HTI increase for shale gas is that wastewater coming from underground is untreated and discharged to the river. Under the worse-case scenario for shale gas, barium and DMF are two biggest contributor which HTI of barium is one order of magnitude larger than DMF. The concentration of barium (median: 164 mg/L) increases two orders of magnitude, which makes a large contribution to HTI of shale gas. Thus, if barium is not well managed on site, shale gas might lose its advantages of its lower human toxicity impact.

Scenario II

In order to conduct a comparable scenario, worst-case for both shale gas and coal are analyzed. The analogous scenario for total release of both fracking fluids and untreated flowback water would be a total release of coal ash. With current air pollution control technology, if the combustion residual storage collapsed, average HTI of coal would be around three to four orders of magnitude higher than shale gas, as shown in Figure 2.1 c). Coal combustion residuals contain mercury, arsenic, barium, chromium, lead which are toxic for aquatic life and human body. Under the worse-case scenario for coal, mercury and arsenic are the first and second largest contributors, which are both carcinogenic and bioaccumulative.

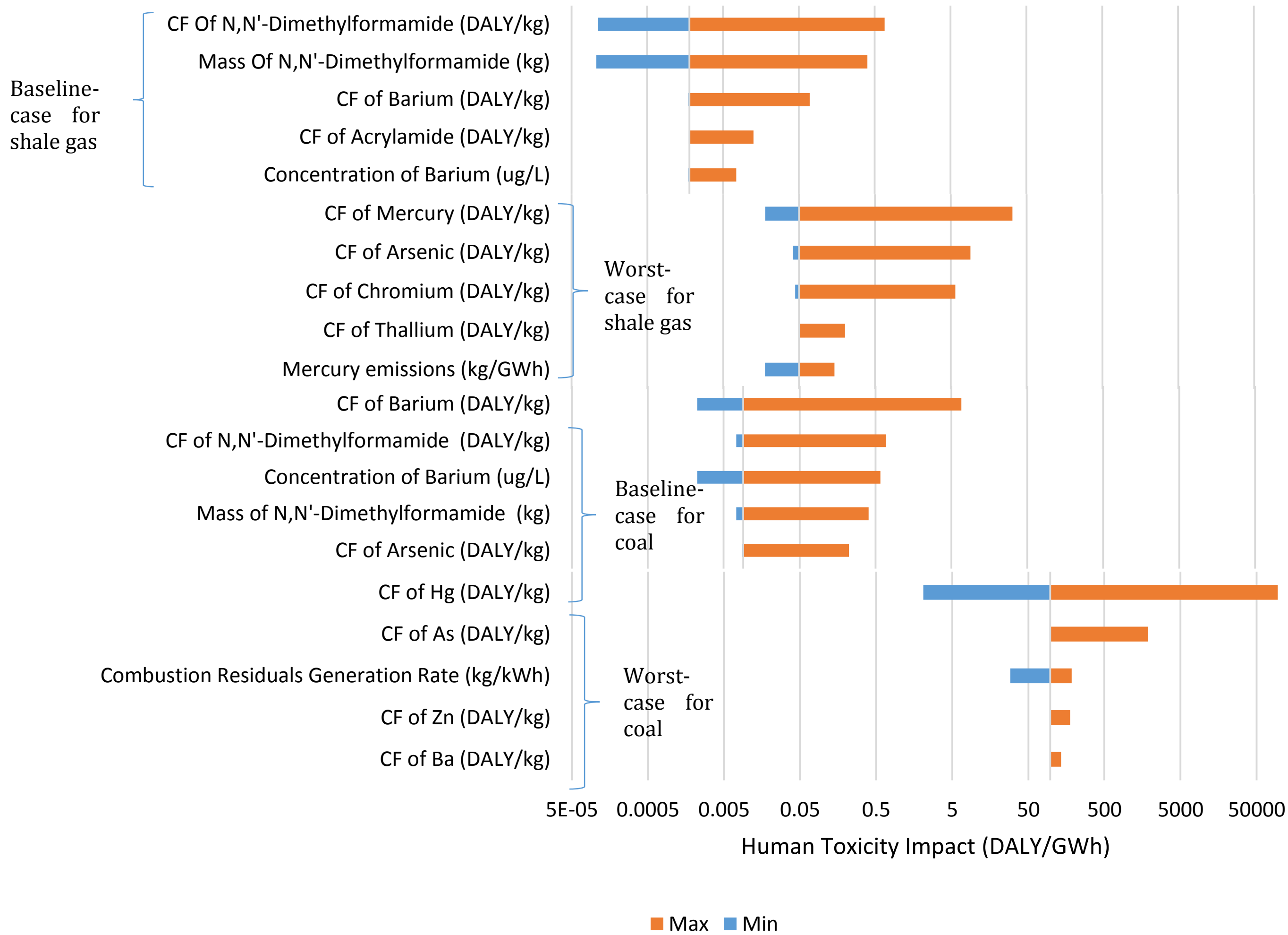

Figure 2.2 Top five biggest contributors for different scenarios (USEtox) are analyzed and shown in tornado plots. CF stands for Characterization Factor. Orange bars show that if one parameter reaches to its maximum value and other parameters stay at the average value, HTI will increase or decrease by a certain level compared with the original value. Blue bars represent the changes of HTI when one parameters decreases to its minimum value but other parameters remain the average value.

Sensitivity analysis, shown in Figure 2.2, gives top five parameters that contribute to either HTI of shale gas or HTI of coal. Compare the baseline-case for both shale gas and coal, if any of the first three parameters for shale gas reaches to its maximum value, HTI of shale gas will be larger than the average HTI of coal. But no matter which parameter for coal reaches to its minimum value, HTI of coal is still larger than the average HTI of shale gas. In terms of the worst-case for both shale gas and coal, no matter which parameter of shale gas reaches to its minimum value, HTI of shale gas is still lower than the average HTI of coal. No matter which parameter leads the change of HTI of coal, it is still larger than the average of shale gas.

Discussion

This study integrates three scenario comparison to first predict HTI of BAU for shale gas and coal;

second, show a valuable method to incorporate extreme scenarios in the analysis that can offer some insights into general trends; third, add on sensitivity analysis to break down the risk source and understand which pollution source contribute the most to HTI of shale gas and coal.

There are two hypothetical cases analyzed for shale gas (baseline-case and worst-case) and two hypothetical cases for coal (baseline-case and worst-case). For shale gas, the worst-case scenario is highly unlikely. On-site chemical storage is controlled by companies and there might be tendency to not fully release spill data due to liability or confidentiality agreements, but this chemical input factor is not expected to significantly affect results. Currently HF wastewater is required to be injected to deep well and monitored by EPA. Also, barium is easily to form $BaSO_4$ by manually adding sulfate in the treatment pond. Thus, wastewater is also unlikely discharged to the river without any treatment. The baseline-case for shale gas is towards but still far off BAU, because the assumption that all chemicals are released in the river has low percentage to happen, (*38*) so it overestimates the HTI of shale gas. As for the fracking fluids that do not flow back above the ground, it will very likely imbibe into the shale because the low permeability shale contains very little free water. (*2*) For coal, without acid mine drainage quantity data because of no baseline water quality value and limited monitoring data, baseline-case for coal is definitely underestimate its HTI. Also, our HTI result for baseline of coal (0.05 DALY/GWh) is smaller than the result from an LCA study from Babbitt and Lindner (0.24 DALY/GWh – 2.2 DALY/GWh). Worst-case for coal is also unlikely to happen, and there are two historical spills, Kingston coal fly ash spill and Duke Energy Dan River coal fly ash spill, happened from 2005 to 2015. Further, a recent analysis of coal ash pond dam integrity rated only 241 of 559 dams as satisfactory, (*53*) prompting regulatory action which may decrease the potential for future unintentional releases of coal ash.

Around HF and coal, there are two currently wide-discussed topics. One is chemicals input in HF, and another one is mercury emission regulation. For HF, based on currently available data, fracking fluids are unlikely mitigated in the shale due to low permeability, and it also has low probability to be directly dumped to the river, however, it does have human toxicity impact. This study and another paper (*23*) show that biocides and corrosion are two main toxic chemical clusters. Companies do not provide information why they use this particular chemical as a corrosion inhibitor, not other chemicals. There are other choices that might provide enough corrosion inhibition function but cause lower human toxicity impact, which companies have not been aware yet. For coal, mercury emissions in air would be the biggest contributor to the variability of the outcome even if power plants conform to air emission regulations. As a bio-accumulative and carcinogenic chemical, the human toxicity impact of it is so high that more stringent emission regulations are necessary to protect residents' health.

We assess HTI of shale gas and coal by USEtox and ReCiPe. Both of them are long-term exposure assessment database, which means near-field exposure is not included, such as occupational air for workers. Although, it isn't a full risk assessment but shows a relative toxicity impact of shale gas and coal. These two different assessment methods give the same result and HTI of each energy source doesn't change over one order of magnitude. However, for Scenario I comparison, we do see the different result of USEtox model and ReCiPe model, because they have different CFs for mercury and barium. Sensitivity analysis shows that barium is the biggest contributor of HTI for shale gas and mercury for coal. CF of mercury in USEtox is 2.18 DALY/kg, which is smaller than that in ReCiPe (0.553 DALY/kg). And ReCiPe has a bigger value of barium (0.0464DALY/kg) than USEtox (0.00644 DALY/kg). Thus, HTI of coal becomes smaller than shale gas by ReCiPe. Also, characterization factors for radioactive elements (mostly Ra) are missing in USEtox, because inhalation and ingestion are two exposure pathway that are considered in USEtox. Even radioactive elements are accidentally emitted to surface water, they have apparently adsorbed and accumulated on the sediments locally at the discharge site. (*27*) If they are eaten by fish and enter to the food chain, the transmission fate and exposure pathway are very different from other chemicals. Sometime they do not fit in long-term exposure assessment. The source of these differences is unclear due to lack of transparency within ReCiPe. Because the scope of an LCA does not allow for a full-scale risk assessment, Life Cycle Impact Assessment (LCIA) uses measures of hazard to compare the relative importance of pollutants within a defined impact category. (*54*) This study conducts an LCIA for shale gas and coal focusing on human toxicity impact. We take the CFs for each chemicals from USEtox and ReCiPe, however, fate factors, exposure pathways, dose-response effect, and severity that are used to calculate the CFs are not addressed in this study. The result of this study could guide future risk assessment to get the actual HTI value of either shale gas or coal. The exposure pathway from shale underground to the surface water and underground water should be well studies, and all chemicals should have their own dose-response effect profile. For coal, acid mine drainage coming from one coal well should be well identified.

As a transaction fuel, only estimating HTI of shale gas isn’t enough. Future work is definitely needed to fill data gap. FracFocus is a voluntary database, which means companies report chemicals input by themselves and there might be a tendency not to disclosure all information. Those chemicals claimed proprietary could be either toxic or non-toxic, and the reason why they are not reported is case by case. For example, fracking companies can’t get that information from a third party contractor. (*55*) Even with limited information of chemical use, there is a knowledge gap about the human toxicity potential of some chemicals. Thus, more toxicology study and health risk modeling are needed in the future. Chemical reaction after pollution emissions is not considered in this study due to data limitation. Elsner and Hoelzer pointed out some chemicals might transform to other products. (*23*) Besides, knowing those chemicals’ reaction conditions and their transmission fate underground are also curtail, because their probability of happening is much more important in environmental assessment, which need more data monitoring and recording. For emissions from coal mining and combustion, methlymercury formed by mercury and organism is highly toxic but hard to know its transformation fraction. PM is another toxic pollutant that formed from air emissions of coal power plant, thus more research about its impact on human health will help people to understand its overall environmental impact and guide future decision-makings. As mentioned before, both shale gas and coal activities lack of monitoring baseline data which makes agencies and researchers impossible to quantify the mass of pollution source and potentially gives companies an excuse to take on their responsibilities.

Appendix

1. Arps equation

Arps equation is being used in this study for estimated ultimate recovery (EUR) of shale gas. It has been the standard for evaluating EUR in oil and gas wells since 1950's (*43*), however, it might be misapplied to ultra-low permeability shale gas wells with constant hyperbolic exponent (b-value) assumption, which make it either overestimate or underestimate EUR. Arps equation only applicable in the boundary-dominated flow regime and conventional gas wells reach this flow regime quickly, which a constant b value is a valid assumption. For shale gas wells, it takes much longer time to reach that condition and makes Arps equation overestimate EUR at the beginning of shale gas production but underestimate EUR for the later years' of production. (*56*) Some scientists created other models, such as numerical models, which is more precise for data they collected. However, we believe those models with limited history data are lack of evidence to show their representatives. Thus, we still use Arps equation in this study for convenient but check shale gas production within ranges. Parameters are provided in Table 1 and the result for each year is listed in Table 2. (*44*)

Arps equation: $q_t = q_i(1 + bD_it)^{-\frac{1}{b}}$

Table S1. Arps Decline Curve Parameters

Parameters	$\boldsymbol{q_i}$ (MMcf)	$\boldsymbol{b}$	$\boldsymbol{D_i}$
Values	4446	1.30	0.11

Table S2. Arps Decline Curve Values for Each Year in 30 Years Lifetime

Month	Pt (MMcf)	Acumulative (MMcf)	Month	Pt (MMcf)	Acumulative (MMcf)	Month	Pt (MMcf)	Acumulative (MMcf)
0	133.38	0	121	14.25344	3585.573	241	8.569505	4795.369
1	120.3482	117.4949	122	14.16837	3598.761	242	8.543018	4803.31
2	109.9156	224.172	123	14.08445	3611.87	243	8.516719	4811.226
3	101.3527	322.0796	124	14.00167	3624.902	244	8.490606	4819.117
4	94.18319	412.7172	125	13.92	3637.858	245	8.464675	4826.985
5	88.08208	497.2179	126	13.83942	3650.739	246	8.438927	4834.828
6	82.81948	576.4607	127	13.7599	3663.545	247	8.413357	4842.648
7	78.22799	651.1422	128	13.68142	3676.278	248	8.387965	4850.444
8	74.18266	721.8245	129	13.60397	3688.939	249	8.362749	4858.216
9	70.5882	788.9682	130	13.52752	3701.528	250	8.337706	4865.965
10	67.37061	852.9561	131	13.45205	3714.047	251	8.312836	4873.692
11	64.4715	914.1099	132	13.37754	3726.496	252	8.288135	4881.395
12	61.84414	972.7025	133	13.30397	3738.877	253	8.263602	4889.075
13	59.45067	1028.968	134	13.23132	3751.189	254	8.239236	4896.732
14	57.26005	1083.109	135	13.15959	3763.435	255	8.215034	4904.367

15	55.24661	1135.3	136	13.08874	3775.614	256	8.190995	4911.98
16	53.38889	1185.697	137	13.01876	3787.729	257	8.167118	4919.57
17	51.66883	1234.435	138	12.94964	3799.778	258	8.1434	4927.138
18	50.07111	1281.635	139	12.88135	3811.764	259	8.119839	4934.685
19	48.58263	1327.404	140	12.81389	3823.687	260	8.096435	4942.209
20	47.19214	1371.837	141	12.74723	3835.547	261	8.073186	4949.712
21	45.88991	1415.022	142	12.68137	3847.347	262	8.050089	4957.194
22	44.66746	1457.036	143	12.61628	3859.085	263	8.027144	4964.654
23	43.5174	1497.949	144	12.55196	3870.763	264	8.004349	4972.092
24	42.43325	1537.827	145	12.48839	3882.382	265	7.981702	4979.51
25	41.40927	1576.726	146	12.42555	3893.943	266	7.959202	4986.907
26	40.44039	1614.701	147	12.36343	3905.445	267	7.936847	4994.283
27	39.52212	1651.801	148	12.30203	3916.89	268	7.914636	5001.638
28	38.65043	1688.071	149	12.24132	3928.278	269	7.892568	5008.973
29	37.82173	1723.552	150	12.1813	3939.611	270	7.87064	5016.287
30	37.03278	1758.282	151	12.12195	3950.888	271	7.848853	5023.581
31	36.28069	1792.298	152	12.06326	3962.11	272	7.827203	5030.855
32	35.56283	1825.632	153	12.00521	3973.278	273	7.80569	5038.109
33	34.87681	1858.314	154	11.94781	3984.392	274	7.784313	5045.343
34	34.22049	1890.374	155	11.89104	3995.454	275	7.76307	5052.557
35	33.5919	1921.838	156	11.83488	4006.463	276	7.74196	5059.752
36	32.98924	1952.73	157	11.77933	4017.42	277	7.720981	5066.927
37	32.41089	1983.075	158	11.72437	4028.326	278	7.700133	5074.082
38	31.85534	2012.893	159	11.67	4039.181	279	7.679414	5081.219
39	31.32121	2042.207	160	11.61621	4049.986	280	7.658822	5088.336
40	30.80724	2071.033	161	11.56298	4060.742	281	7.638357	5095.434
41	30.31227	2099.392	162	11.51031	4071.448	282	7.618017	5102.513
42	29.83521	2127.3	163	11.45819	4082.106	283	7.597802	5109.573
43	29.37507	2154.773	164	11.40661	4092.715	284	7.577709	5116.615
44	28.93094	2181.827	165	11.35556	4103.277	285	7.557739	5123.638
45	28.50195	2208.475	166	11.30503	4113.792	286	7.537889	5130.642
46	28.08732	2234.732	167	11.25502	4124.26	287	7.518158	5137.629
47	27.6863	2260.611	168	11.20551	4134.682	288	7.498546	5144.596
48	27.29821	2286.123	169	11.1565	4145.058	289	7.479051	5151.546
49	26.92241	2311.281	170	11.10798	4155.389	290	7.459672	5158.478
50	26.5583	2336.096	171	11.05995	4165.675	291	7.440409	5165.392
51	26.20532	2360.578	172	11.01239	4175.917	292	7.421259	5172.288
52	25.86294	2384.738	173	10.96529	4186.115	293	7.402222	5179.166
53	25.53069	2408.584	174	10.91866	4196.269	294	7.383298	5186.027
54	25.20809	2432.127	175	10.87248	4206.381	295	7.364484	5192.87
55	24.89471	2455.375	176	10.82675	4216.449	296	7.34578	5199.696
56	24.59015	2478.336	177	10.78145	4226.476	297	7.327185	5206.504
57	24.29403	2501.018	178	10.7366	4236.46	298	7.308698	5213.295

58	24.00598	2523.429	179	10.69216	4246.404	299	7.290318	5220.069
59	23.72567	2545.577	180	10.64815	4256.306	300	7.272043	5226.827
60	23.45277	2567.467	181	10.60456	4266.167	301	7.253874	5233.567
61	23.18699	2589.108	182	10.56137	4275.988	302	7.235809	5240.29
62	22.92803	2610.506	183	10.51858	4285.77	303	7.217847	5246.997
63	22.67563	2631.666	184	10.47619	4295.512	304	7.199988	5253.687
64	22.42953	2652.595	185	10.43419	4305.214	305	7.182229	5260.36
65	22.18949	2673.298	186	10.39258	4314.878	306	7.164571	5267.017
66	21.95528	2693.781	187	10.35134	4324.503	307	7.147013	5273.658
67	21.72667	2714.05	188	10.31049	4334.091	308	7.129553	5280.283
68	21.50347	2734.109	189	10.27	4343.64	309	7.112191	5286.891
69	21.28547	2753.963	190	10.22987	4353.153	310	7.094926	5293.483
70	21.07249	2773.617	191	10.1901	4362.628	311	7.077757	5300.06
71	20.86435	2793.076	192	10.15069	4372.066	312	7.060683	5306.62
72	20.66087	2812.344	193	10.11162	4381.468	313	7.043704	5313.165
73	20.4619	2831.425	194	10.0729	4390.834	314	7.026818	5319.694
74	20.26729	2850.324	195	10.03452	4400.164	315	7.010025	5326.207
75	20.07688	2869.044	196	9.996473	4409.458	316	6.993324	5332.705
76	19.89053	2887.589	197	9.958756	4418.718	317	6.976715	5339.187
77	19.70812	2905.963	198	9.921365	4427.942	318	6.960196	5345.654
78	19.52951	2924.169	199	9.884295	4437.133	319	6.943766	5352.105
79	19.35458	2942.212	200	9.847542	4446.288	320	6.927426	5358.542
80	19.18321	2960.093	201	9.811102	4455.41	321	6.911173	5364.963
81	19.01529	2977.818	202	9.774971	4464.498	322	6.895008	5371.369
82	18.85071	2995.388	203	9.739145	4473.553	323	6.87893	5377.76
83	18.68937	3012.807	204	9.703619	4482.575	324	6.862938	5384.137
84	18.53118	3030.077	205	9.668389	4491.564	325	6.847031	5390.498
85	18.37603	3047.202	206	9.633452	4500.52	326	6.831208	5396.845
86	18.22383	3064.185	207	9.598805	4509.444	327	6.81547	5403.178
87	18.07451	3081.027	208	9.564442	4518.336	328	6.799814	5409.495
88	17.92796	3097.733	209	9.530362	4527.196	329	6.784241	5415.798
89	17.78413	3114.304	210	9.496559	4536.025	330	6.76875	5422.087
90	17.64292	3130.742	211	9.463031	4544.822	331	6.75334	5428.362
91	17.50426	3147.05	212	9.429774	4553.589	332	6.73801	5434.622
92	17.36808	3163.231	213	9.396784	4562.324	333	6.72276	5440.868
93	17.23432	3179.287	214	9.364059	4571.03	334	6.707589	5447.099
94	17.1029	3195.22	215	9.331594	4579.705	335	6.692497	5453.317
95	16.97376	3211.032	216	9.299387	4588.35	336	6.677483	5459.521
96	16.84684	3226.725	217	9.267435	4596.965	337	6.662546	5465.711
97	16.72209	3242.301	218	9.235734	4605.551	338	6.647685	5471.887
98	16.59944	3257.762	219	9.204282	4614.107	339	6.632901	5478.05
99	16.47884	3273.111	220	9.173075	4622.634	340	6.618192	5484.198
100	16.36024	3288.349	221	9.14211	4631.133	341	6.603558	5490.333

101	16.24358	3303.477	222	9.111384	4639.603	342	6.588998	5496.455
102	16.12882	3318.498	223	9.080895	4648.044	343	6.574511	5502.563
103	16.0159	3333.414	224	9.05064	4656.457	344	6.560098	5508.657
104	15.90479	3348.225	225	9.020615	4664.842	345	6.545757	5514.739
105	15.79543	3362.934	226	8.990819	4673.2	346	6.531488	5520.807
106	15.68779	3377.543	227	8.961247	4681.53	347	6.517291	5526.861
107	15.58182	3392.052	228	8.931899	4689.833	348	6.503164	5532.903
108	15.47748	3406.464	229	8.902771	4698.108	349	6.489107	5538.932
109	15.37474	3420.78	230	8.87386	4706.357	350	6.47512	5544.947
110	15.27355	3435.001	231	8.845165	4714.578	351	6.461202	5550.95
111	15.17388	3449.128	232	8.816681	4722.774	352	6.447353	5556.94
112	15.07569	3463.165	233	8.788408	4730.943	353	6.433572	5562.916
113	14.97895	3477.11	234	8.760343	4739.086	354	6.419859	5568.881
114	14.88363	3490.967	235	8.732483	4747.202	355	6.406212	5574.832
115	14.78969	3504.735	236	8.704826	4755.294	356	6.392632	5580.771
116	14.69711	3518.418	237	8.677369	4763.359	357	6.379118	5586.697
117	14.60585	3532.014	238	8.650111	4771.399	358	6.36567	5592.611
118	14.51587	3545.527	239	8.623049	4779.414	359	6.352287	5598.512
119	14.42717	3558.957	240	8.596181	4787.404	360	6.338968	5604.401
120	14.3397	3572.305						

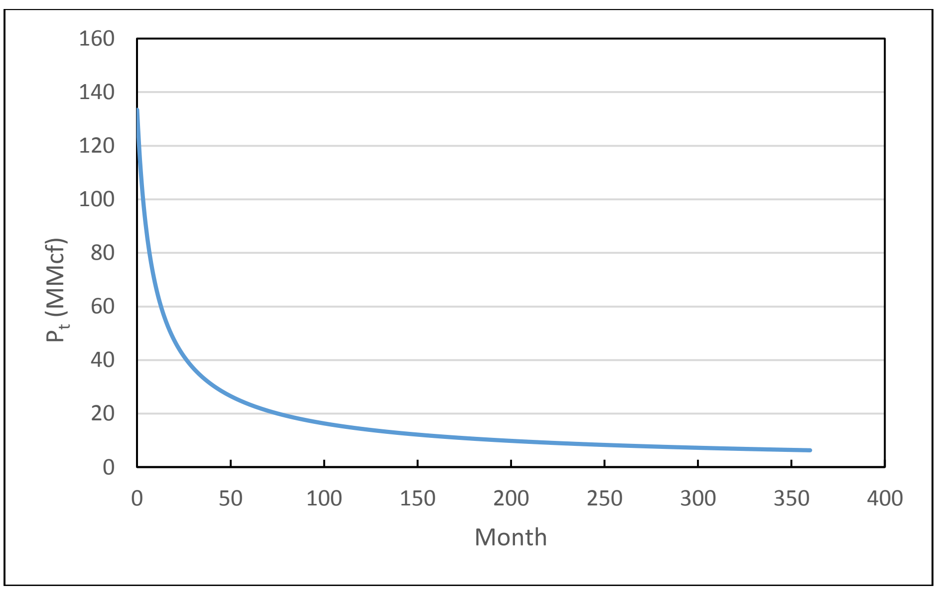

Figure 1. Arps Decline Curve of Shale Gas Production in Marcellus Basin

2. Human Toxicity Impact

$$Human\ Toxicity\ Potential = \frac{Characterization\ Factor \times \frac{Mass\ emission}{mass\ fuel}}{\frac{GWh\ electricity\ produced}{mass\ fuel}}$$

$$HT_{CI,i} = \frac{CF_{CI,i} \times m_{CI,i}}{\overline{V_g} \times E}$$

$$HT_{F,i} = \frac{CF_{F,i} \times m_{F,i}}{\overline{V_g} \times E}$$

$$HT_{Hg} = CF_{Hg} \times \overline{R_{Hg}}$$

$$HT_{CR} = CF_{CR} \times \overline{R_{CR}}$$

$$HT_{NO_x,i} = \frac{m_{NO_x,i}}{EG_i}$$

$$HT_{SO_2,i} = \frac{m_{SO_2,i}}{EG_i}$$

where HT is the human toxicity impact characterized by DALY at endpoint level. CF is the characterization factor of chemicals input characterized by DALY/kg; the subscript i represents each individual well; the subscript Cl I represents chemicals input; F represents flowback water; Hg represents mercury emission from the coal-fired power plants; CR represents combustion residuals coming out of the ponds. m is the total mass of each chemical (kg). $\overline{V_g}$ is the average volume of shale gas produced during a certain period (Mcf). E is the energy efficiency (kWh/Mcf). $\overline{R_{Hg}}$ is the average mercury emission rate (kg/kWh). $\overline{R_{CR}}$ is the average combustion residuals discharge rate; NO_x and SO_2 represents the nitrogen oxide and sulfur dioxide emissions in the power plant; EG represents electricity generation value (kWh).

3. Data list for baseline scenario

Table S3. Detailed assumptions for shale gas and coal

Parameter	Unit	Value	Range	Reference
Average water injected to the well	m^3/well	13093.77	3500-26000	(*57*)
Flowback water percentage share of injected water	%	15	10-15	(*20*), (*2*)
Produced water percentage share of injected water	%	5	1-7	(*20*)
Shale gas efficiency	Mcf / kWh	0.0101	N/A	(*58*)
Shale gas well lifetime span	year	15	5-30	(*10*)
Shale gas production volume	Mcf	4256	2000-7770000	(*44*)
Mercury emission per kWh electricity	kg/kWh	13608	4536-58967	(*59*)
NO_x emission per kWh electricity from natural gas power plant	kg/kWh	4.95E-5	2.54E-5 – 1.60E-3	(*60*)
SO_2 emission per kWh electricity from natural gas power plant	kg/kWh	2.61E-6	1.02E-6 – 6.16E-6	(*60*)

NO_x emission per kWh electricity from coal power plant	kg/kWh	0.0011	0.00040-0.0027	(*60*)
SO_2 emission per kWh electricity from coal power plant	kg/kWh	0.0038	0.00016-0.014	(*60*)

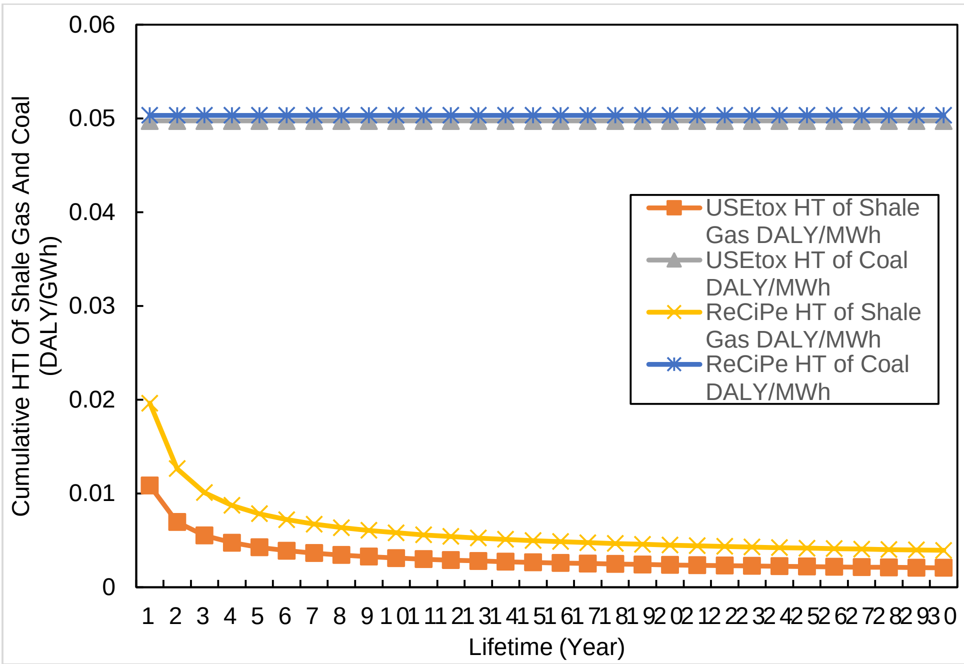

Figure S2. HTI of shale gas and coal during 30 years lifetime for baseline scenario comparison

4. Characterization factors from USEtox and ReCiPe

Table S4. Human Toxicity Characterization Factors for Chemicals Input during HF

Cas	Ingredient Name	CF-Usetox (Daly/Kg)	CF-Recipe (Daly/Kg)	Total Mass (Kg)	Purpose	Dose-Response Category
107-21-1	Ethylene Glycol	1.01e-09	4.80e-09	1211340.37	Corrosion Inhibitor	Non-Carcinogen
67-56-1	Methanol	9.06e-10	3.80e-09	66688.92	Corrosion Inhibitor	Non-Carcinogen
107-19-7	Propargyl Alcohol	1.39e-07	2.18e-07	7990.48	Corrosion Inhibitor	Non-Carcinogen
111-76-2	Ethylene Glycol, Monobutyl Ether	3.14e-08	5.55e-08	3564.77	Non-Emulsifier	Carcinogen
68-12-2	N,N'-Dimethylformamide	2.29e-07	4.15e-07	3105653.09	Corrosion Inhibitor	Non-Carcinogen
50-00-0	Formaldehyde	7.74e-08	3.73e-06	1968.48	Corrosion Inhibitor	Carcinogen
64-17-5	Ethanol	9.86e-10	1.41e-10	25413.12	Biocide	Carcinogen
79-06-1	Acrylamide	7.24e-06	3.40e-06	1579.89	Friction Reducer	Carcinogen
111-46-6	Diethylene Glycol	5.02e-09	2.56e-09	2456.59	Corrosion Inhibitor	Carcinogen

62-56-6	Acetophenone	1.74e-09	4.87e-08	211.95	Corrosion Inhibitor	Carcinogen
98-86-2	Thiourea	1.53e-07	1.16e-08	325.26	Corrosion Inhibitor	Non-Carcinogen
104-76-7	2-Ethyl-1-Hexanol	1.05e-08	1.38e-08	11321.08	Combination/Iron Control	Carcinogen

5. Coal ash failure in Kingston, 2008

In this study we took data from Kingston coal ash spill as part of the worst-case scenario for coal. (*61*) The characterization factor for each chemical in USEtox was weighted (1:1) from fresh water compartment and agriculture soil compartment due to lack of sediment compartment information. The characterization factor for each chemical in ReCiPe was assumed the same as the value in industrial soil compartment. Remediation efforts took place in 2009 and 2010 leaving 0.18 million m^3 of ash in Emory River. We assumed the density of ash is 1500 kg/m^3 and assessing the HTI of the ash left in Emory River after remediation.

Table S5. Components in Coal Combustion Residuals Spill

Component	Mass (kg) (*61*)	CF-USEtox (DALY/kg)	CF-ReCiPe (DALY/kg)
Al	1.28E+06	na	na
As	1.92E+04	2.46E-01	2.42E-01
Ba	7.57E+04	4.42E-02	4.19E-02
Be	7.56E+02	2.52E-03	2.20E-03
Cd	5.40E+00	2.20E-03	4.01E-03
Ca	5.15E+05	-	na
Cr	3.48E+03	9.77E-09	1.81E-08
Co	1.67E+03	na	na
Cu	8.18E+03	5.43E-06	6.89E-06
Fe	0	na	na
Pb	6.75E+02	9.13E-04	1.14E-03
Li	5.21E+03	-	na
Mg	1.09E+05	-	na
Mn	0	8.97E-03	8.97E-03
Mo	5.13E+02	1.67E-01	1.59E-01
Ni	5.02E+03	1.32E-04	1.30E-04
Se	0	2.79E+00	2.64E+00
Sr	5.24E+04	na	na
V	1.51E+04	1.03E-02	9.89E-03
Zn	2.89E+03	1.89E-04	2.25E-04
Hg	2.87E+04	1.66E-01	5.53E-01

6. Water Effluent from Combustion Residual Impoundment

Table S6 Components in Combustion Residuals Impoundment (*32*)

	Mass (kg)	CF-USEtox (DALY/kg)	CF-ReCiPe (DALY/kg)
Manganese	3831	na	0.00897

Strontium	33619	na	-
Lithium	4728	-	-
Boron	278424	-	-
Aluminium	4554	na	-
Vanadium	289	0.006180039	0.0107
Chromium	73	1.249043632	1.43E-09
Cobalt	41	na	8E-23
Nickel	224	0.005063657	0.000133
Arsenic	664	0.435420107	0.25
Selenium	772	0	2.93
Rubidium	208	-	-
Molybdenum	1303	0.000225558	0.174
Cadmium	3	0.057913497	0.000386
Antimony	87	0.001600772	0.0218
Thallium	28	0.144918664	0.203

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