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Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on “toxic” chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

Reviews of Environmental Contamination and Toxicology [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

Bulletin of Environmental Contamination and Toxicology (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects of environmental contamination and associated (eco)toxicological consequences. Such articles facilitate the often complex task of accessing and interpreting cogent scientific data within the confines of one or more closely related research fields.

In the 50+ years since *Reviews of Environmental Contamination and Toxicology* (formerly *Residue Reviews)* was first published, the number, scope, and complexity of environmental pollution incidents have grown unabated. During this entire period, the emphasis has been on publishing articles that address the presence and toxicity of environmental contaminants. New research is published each year on a myriad of environmental pollution issues facing people worldwide. This fact, and the routine discovery and reporting of emerging contaminants and new environmental contamination cases, creates an increasingly important function for *Reviews.* The staggering volume of scientific literature demands remedy by which data can be synthesized and made available to readers in an abridged form. *Reviews* addresses this need and provides detailed reviews worldwide to key scientists and science or policy administrators, whether employed by government, universities, nongovernmental organizations, or the private sector.

There is a panoply of environmental issues and concerns on which many scientists have focused their research in past years. The scope of this list is quite broad, encompassing environmental events globally that affect marine and terrestrial ecosystems; biotic and abiotic environments; impacts on plants, humans, and wildlife; and pollutants, both chemical and radioactive; as well as the ravages of environmental disease in virtually all environmental media (soil, water, air). New or enhanced safety and environmental concerns have emerged in the last decade to be added to incidents covered by the media, studied by scientists, and addressed by governmental and private institutions. Among these are events so striking that they are creating a paradigm shift. Two in particular are at the center of ever increasing media as well as scientific attention: bioterrorism and global warming. Unfortunately, these very worrisome issues are now superimposed on the already extensive list of ongoing environmental challenges.

The ultimate role of publishing scientific environmental research is to enhance understanding of the environment in ways that allow the public to be better informed or, in other words, to enable the public to have access to sufficient information. Because the public gets most of its information on science and technology from internet, TV news, and reports, the role for scientists as interpreters and brokers of scientific information to the public will grow rather than diminish. Environmentalism is an important global political force, resulting in the emergence of multinational consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the twenty-first century involve a consortium of technologists and environmentalists, or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, because the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists. New legislation that will deal in an appropriate manner with this challenge is currently in the making or has been implemented recently, such as the REACH legislation in Europe. These regulations demand scientifically sound and documented dossiers on new chemicals.

Reviews publishes synoptic articles designed to treat the presence, fate, and, if possible, the safety of xenobiotics in any segment of the environment. These reviews can be either general or specific, but properly lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, (eco)toxicology, and regulation. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems may also be appropriate.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are likely in preparation or planned. The field is so very large and the interests in it are so varied that the editor and the editorial board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of anthropogenic chemicals in our surroundings. Thus, manuscripts may encompass case studies from any country. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their scope.

Manuscripts are often contributed by invitation. However, nominations for new topics or topics in areas that are rapidly advancing are welcome. Preliminary communication with the Editor-in-Chief is recommended before volunteered review manuscripts are submitted. *Reviews* is registered in WebofScience™.

Inclusion in the Science Citation Index serves to encourage scientists in academia to contribute to the series. The impact factor in recent years has increased from 2.5 in 2009 to 7.0 in 2017. The Editor-in-Chief and the Editorial Board strive for a further increase of the journal impact factor by actively inviting authors to submit manuscripts.

Amsterdam, The Netherlands Pim de Voogt
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Investigating the Potential Toxicity of Hydraulic Fracturing Flowback and Produced Water Spills to Aquatic Animals in Freshwater Environments: A North American Perspective

Erik J. Folkerts, Greg G. Goss, and Tamzin A. Blewett

Contents

Abstract Unconventional methods of oil and natural gas extraction have been a growing part of North America's energy sector for the past 20–30 years. Technologies such as horizontal hydraulic fracturing have facilitated the exploitation of geologic reserves that were previously resistant to standard drilling approaches. However, the environmental risks associated with hydraulic fracturing are relatively understudied. One such hazard is the wastewater by-product of hydraulic fracturing processes: flowback and produced water (FPW). During FPW production, transport, and storage, there are many potential pathways for environmental exposure. In the current review, toxicological hazards associated

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with FPW surface water contamination events and potential effects on freshwater biota are assessed. This review contains an extensive survey of chemicals commonly associated with FPW samples from shale formations across North America and median 50% lethal concentration values (LC_{50}) of corresponding chemicals for many freshwater organisms. We identify the characteristics of FPW which may have the greatest potential to be drivers of toxicity to freshwater organisms. Notably, components associated with salinity, the organic fraction, and metal species are reviewed. Additionally, we examine the current state of FPW production in North America and identify the most significant obstacles impeding proper risk assessment development when environmental contamination events of this wastewater occur. Findings within this study will serve to catalyze further work on areas currently lacking in FPW research, including expanded whole effluent testing, repeated and chronic FPW exposure studies, and toxicity identification evaluations.

Keywords Formations · Hazards · Invertebrates · LC_{50} · Major ions · Metals · Natural gas · Oil · Organics · PAH · Regulation · Salts · Spills · Trace metals · Vertebrates · VOC · Wastewater

Abbreviations

AB	Alberta
AER	Alberta Energy Regulator
Ag	Silver
AhR	Aryl hydrocarbon receptor
Ba	Barium
BC	British Columbia
BCOGC	British Columbia Oil and Gas Commission
BTEX	Benzene, toluene, ethylbenzene, and xylene
Ca	Calcium
Cd	Cadmium
Cu	Copper
DBCM	Dibromochloromethane
DOC	Dissolved organic carbon
ER	Estrogen receptor
Fe	Iron
FPW	Flowback and produced water
HCB	Hexachlorobenzene
HPF	Hours post fertilization
HPG/I	Hypothalamic-pituitary-gonadal/interrenal
ILCM	Interlamellar cell mass
K	Potassium
KOW	Octanol-water partitioning coefficient
LC_{50}	Lethal concentration causing 50% Mortality
Mg	Magnesium

Mn	Manganese
MYA	Million years ago
Na	Sodium
Ni	Nickel
NOS	Nitric oxide synthase
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
PCP	Pentachlorophenol
PXR	Pregnane X receptor
ROS	Reactive oxygen species
Sr	Strontium
TDS	Total dissolved solid
Tl	Thallium
UOG	Unconventional oil and gas
VOC	Volatile organic compound
WET	Whole effluent toxicity
Zn	Zinc

1 Introduction

Extraction of hydrocarbons from unconventional resources is increasing globally as a result of technological advances in horizontal drilling (Gagnon et al. 2016; Vengosh et al. 2014). Hydraulic fracturing is one such advance where chemically formulated fluids are used to fracture low permeability formations under high pressure and temperature (Stringfellow et al. 2014). This process increases the permeability of shale, tight sands, coalbeds, and other gas and oil containing strata, facilitating extraction of hydrocarbon resources from reserves that would otherwise be uneconomic (Stringfellow et al. 2014). Hydraulic fracturing fluids are injected over a short period of time and use large quantities of water per well injection (10,000–100,000 m^3). Injected fluids are comprised of chemical additives that maximize efficiency and output of oil and gas from any given well. These additives include proppants (e.g., ceramic beads, sand – to prevent fracture reclosure), biocides (to prevent microbial degradation of end product resources and maintain well viability), gelling and foaming agents, pH adjustors, clay stabilizers, and surfactants (Ferrer and Thurman 2015; DiGiulio and Jackson 2016; Lester et al. 2015; FracFocus.org). When pressure along the length of the fracture is released, these complex chemical mixtures of hydraulic fracturing fluid return to the surface, and this fluid is termed either flowback or produced water. The delineation of "flowback" versus "produced water" is often subject to well operator discretion. Flowback typically is considered the earliest fluid which returns to the surface and which most closely resembles the composition of the initial injection fluid.

Produced water is the fluid returning from the subterranean environment following longer periods of well production. This fluid is often saline in nature and contains high gas and oil content, which is then operationally separated (U.S. EPA 2016). The distinction between these two types of fluid is not clear, since mixing occurs in the formation, so for the purposes of this review, we will refer to the hydraulic fracturing wastewater as flowback and produced water (FPW) (Stringfellow et al. 2014) with the recognition that toxicological properties of FPW change over the course of flowback production. FPW is a chemically complex heterogeneous mixture that contains highly variable concentrations of organic compounds (e.g., polycyclic aromatic hydrocarbons, PAHs), naturally occurring radioisotopes (e.g., radium), ions (e.g., calcium, magnesium, chloride, sodium, potassium), metals (e.g., barium, thallium, lead), and transformation products resulting from chemical reactions under high temperature and high pressure (DiGiulio and Jackson 2016; He et al. 2017a; Lester et al. 2015) (further expansion in Sect. 2). The specific composition of any given FPW is unique, depending on many factors including the geology of the formation, well shut-in length, phase of flowback collection, and the composition of the initial fracturing fluid additives used for operation (Alessi et al. 2017; Goss et al. 2015; Stringfellow et al. 2017). FPW may be recycled but must eventually be disposed of.

It is estimated that in the USA, unconventional production of natural gas will account for nearly half of newly developed gas production by 2035 (Gagnon et al. 2016). Considering this expected rise in unconventional oil and gas (UOG) activity and the large quantities of FPW created from these processes, management strategies for FPW and potential hazards to the environment are two growing concerns facing the industry and regional governments. One of the key risks associated with hydraulic fracturing is the potential for spills during the generation and transport of large volumes of FPW. Such risks include ground and surface water contamination during pipeline leaks, truck transportation, and injection well integrity issues (Ferrar et al. 2013). Determination of ecological impacts of FPW is considered a top science priority to inform energy policy, conservation, and management of natural systems (Jones et al. 2015). As such, government, industry, landowners, and environmental groups have scrutinized the current methods of storage, transportation, and remediation protocols when spills/leaks occur of this wastewater (Boudet et al. 2014; Gehman et al. 2016; Theodori et al. 2014).

Despite rigorous regulation and controls in all North American jurisdictions on the handling of FPW, spills still occur. Depending on the state/province, a spill or release of FPW warranting report can vary in terms of volume of spill, spill type, and time required to report a spill. For example, in both North Dakota and Colorado, spills escaping secondary containment of $\geq$42 gal must be reported, with written report of said spills mandated within at least 10 days (Patterson et al. 2017). In Pennsylvania, however, spills of $\geq$5–15 gal (depending on FPW TDS measurements) are required within 24 h, whereas in New Mexico, only spills $\geq$210 gal require written notification within 15 days (Patterson et al. 2017). In the province of Alberta, Canada, the Alberta Energy Regulator (the main energy policy and regulating agency in the province) requires spills of $\geq$2000 L (~ 530 gal) to be reported within 24 h (Alberta Energy Regulator n.d.; AER). Regarding spill frequency, in Alberta, an estimated >2,500 FPW spills occurred from 2005 to 2012 with more than 113 of those spills entering into freshwater lakes and streams (Alessi et al. 2017; Goss et al. 2015). Analysis of data from 2005 to 2014 representing >30,000 UOG wells in the states of Colorado, North Dakota, Pennsylvania, and New Mexico showed that 50% of spills were associated with storage or transport of FPW and that 2–16% of wells reported a spill every year, the largest singular FPW spill recorded at 3,756 m^3 (Patterson et al. 2017). However, in this same study, it was found overall that across the three states of Colorado, North Dakota, and Pennsylvania, annual spill rates are either being sustained or decreasing, with only New Mexico showing an increasing annual spill rate (Patterson et al. 2017). With increased use of UOG technologies on the rise recently, however, it is only expected that spills of FPW will continue and become more prevalent. Furthermore, risks associated with FPW are not only from spills but from direct application for dust suppression or de-icing on roads. Currently, 13 states in the USA allow spreading of FPW on roads as an inexpensive alternative to other dust suppressants (Tasker et al. 2018). FPW released to the environment in this manner has the potential to leach from roads during rain events into ground and surface water and cause toxicity to aquatic biota. In Northern Pennsylvania alone, over 280,000 L of FPW was spread on roads in 2015 (Pennsylvania Department of Environmental Protection 2016) resulting in a mean radium concentration of 14.5 pCi/L in surface waters associated with the contaminated roadways, significantly higher than national recommended regulatory limits for radium in drinking water (5 pCi/L) (Tasker et al. 2018).

This review summarizes the known chemical composition of FPW and characterizes the risks to the aquatic environment associated with FPW spills. We have collected and collated FPW characterization data from multiple independent published academic, government, and industry sources on North American formations used for UOG practices and identify three largest and most commonly observed components of FPW which pose the greatest risk to aquatic animals in a spill event. These components include organics, trace metals, and major ions. After identifying these common components, the toxicity of specific chemicals pertaining to these components is further investigated by reviewing respective published lethal and sublethal effects for each chemical. The few studies performed to date which have specifically examined the toxicity of FPW (or simulated FPW) are also reviewed and used to identify the progress of FPW research on freshwater biota and to highlight specific areas requiring further investigation.

2 FPW Chemical Characterization

In the current review, three major classes of chemical species were taken into consideration when analyzing the composition of FPW samples: major ions and other general water characteristics, organic constituents, and trace metals. Although radioactivity associated with FPW has also been determined to be of potential concern to natural environments (Haluszczak et al. 2013; Tasker et al. 2018), analysis of FPW radioactivity was not included in this review. However, a table recording types and levels of radioactivity associated with FPW can be found in the Supplemental Information (SI Table 1). Furthermore, we have restricted our analyses to only those constituents that are commonly reported across studies of FPW composition from North American hydraulic fracturing operations. In total, 15 different sources of detailed chemical analysis of strictly FPW (not affected surface waters or effluent discharges) were compiled to create a single database of over 5,000 data points of targeted inorganic and organic chemicals. These sources can be found in Table 1. It should be noted that the analyzed FPW samples detailed in the literature vary with respect to the timing of collection (flowback period sampled), well location, and shale formation being exploited – all factors which influence FPW chemistry. Indeed, many reports do not offer sufficient or complete details regarding these variables. Consequently, it is therefore acknowledged that the current review is not able to offer detail regarding how the chemical composition and toxicity of FPW samples differ with respect to time spent in the well or source geology. For information on hydraulic fracturing-associated wastewaters from drilling operations in other non-North American formations and on potential other toxicities pertaining to the initial fracturing fluid used to induce fractures, please see reviews by Faber et al. (2017) and Annevelink et al. (2016).

2.1 Major Ions

Cations and anions/salt-related ions (see Table 2) are major components of FPW and are primarily responsible for the high total dissolved solid (TDS) concentrations that are often observed in FPW samples. During the fracturing process, many classes of chemical compounds present in the initial fracturing fluid pumped down the wellbore (e.g., acids, breakers, and stabilizers) contain ionic chemical species that enhance operational efficiency and maximize resource recovery (FracFocus.org). These include chemicals such as hydrochloric acid (used to dissolve minerals and initiate fissure formation), sodium and calcium chloride (breakers used to stabilize geogenic products and clay formations), magnesium peroxide (a breaker used to delay gel break down), and many others. These ions, following parent compound reactions, reside in the formation fluid until they are brought back up to the surface in FPW.

However, another source of salt ionic species contributing to the commonly seen high FPW TDS concentrations is the geological environment being targeted/exploited during hydraulic fracturing activities. During the mid-late Cretaceous era (~100 million years ago; MYA), North America was divided into two land masses by a large inland sea which stretched from the Gulf of Mexico to the Arctic Ocean (Nicholls and Russell 1990). Correspondingly, many of the sedimentary formations exploited for hydraulic fracturing purposes have a marine origin,

Table 1 References used for compiling chemical characterization data

Reference	Type of document	Analytical methods and QA/QC stated?	Location/ formation of FPW sampled	Time period of FPW sample(s) (days post-well stimulation)
US EPA Atlas response_211 419 (2015)	Analytical study report	Yes	Unknown (Marcellus suspected)	Unknown
Blauch et al. (2009)	Regional meeting paper	No	Pennsylvania/ Marcellus	0–55
Blewett et al. (2017a)	Academic paper	Yes	Alberta/ Duvernay	10
DEP_TENORM (2016)	Analytical study report	Yes	Pennsylvania/ Marcellus	Unknown
Dresel and Rose (2010)	Geological survey report	Yes	Pennsylvania/ Marcellus	Unknown
Hayes (2009)	Analytical study report	Yes	Pennsylvania/ Marcellus	0, 1, 5, 14, and 90
He et al. (2017a)	Academic paper	Yes	Alberta/ Duvernay	7
Lauer et al. (2016)	Academic paper	Yes/No	North Dakota/ Bakken	Unknown
Lester et al. (2015)	Academic paper	Yes	Colorado/Denver-Julesburg Basin	Unknown
Maguire-Boyle and Barron (2014)	Academic paper	Yes	Pennsylvania/ Marcellus Texas/Eagle Ford Barnett/New Mexico	Unknown
NYS_DEC (2015)	Environmental impact statement proceeding	Yes/No	Pennsylvania – West Virginia/ Marcellus	Unknown
DEP_Inorganics Report (2010)	Analytical study report	No	Unknown (Marcellus suspected)	Unknown
Rosenblum et al. (2017a)	Academic paper	Yes	Colorado/ Niobrara	1, 4, 7, 15, 22, 80, 130, 220, and 405
Rosenblum et al. (2017b)	Academic paper	Yes	Colorado/ Niobrara	1, 4, 7, 15, 22, 55, 80, 130, and 220
Ziemkiewicz et al. (2014)	Academic paper	Yes	Pennsylvania/ Marcellus	Unknown

Table 2 General water quality and ion concentrations in hydraulic fracturing flowback and produced water samples and current acute (and chronic) guideline concentrations for the protection of freshwater aquatic life according to Canadian Environmental Quality Guidelines (CEQ) and the US Environmental Protection Agency (USEPA)

Chemical	$\overline{X}$ conc.	Median conc.	Range	*N*	CEQ guidelines		USEPA guidelines	
					Acute	Chronic	Acute	Chronic
Bromide	610	472	0.2–2,240	147	ND	ND	ND	ND
Calcium	9,252	7,630	35.2–41,600	164	ND	ND	ND	ND
Chloride	60,293	43,800	64.2–207,000	193	640	120	860	230
Magnesium	982	710	7.1–13,000	164	ND	ND	ND	ND
Manganese	9	4	0–96.5	160	ND	ND	ND	ND
Potassium	705	253	2.7–17,043	148	ND	ND	ND	ND
Sodium	26,669	21,510	45.9–95,500	165	ND	ND	ND	ND
Sulfate	94	46	0–1,010	167	ND	ND	ND	ND
TDS	108,562	91,405	680–345,000	148	ND	ND	ND	ND
Nitrate	2.049	1.3	0.081–15.9	74	550	13	ND	ND
Nitrite	12.03	4.7	0.045–146	72	ND	60	ND	ND
Nitrogen (total)	116	96	5.6–498	69	ND	ND	ND	ND
Carbon (total)[a]	1,200	110	1.2–58,550	77	ND	ND	ND	ND
pH	6.3	6.5	3.4–10.1	126	ND	6.5–9.0	ND	6.5–9.0

ND no data, *N* number of collective samples used to establish range. All values in mg/L

[a] Carbon (total) includes measurements of total organic carbon, total carbon, and dissolved organic carbon

and as a consequence, formation waters and FPW from these formations following natural resource production contain high levels of major ions/salts (Connolly et al. 1990; Kahrilas et al. 2016; Li et al. 1997; Rice 2003; Zhuoheng and Osadetz 2013).

2.2 *Trace Metals*

FPW metal profiles depend greatly on the geology of the formation being exploited. As seen in Table 3, numerous different trace metals may be present in FPW and at varying concentrations. The trace metals present in FPW which will be discussed in this section are from multiple different chemical groups, including the alkali and alkaline earth metals (e.g., barium and strontium – both of which are commonly found at high concentrations in FPW), classically defined "transition" metals (e.g., iron, zinc, cadmium, etc.), post-"transition" metals (e.g., aluminum, lead, thallium, etc.), and metalloids (e.g., boron, arsenic, etc.). Due to their toxicity at relatively low concentrations (Wood 2012a), many of these metals may pose significant hazards to aquatic systems if present (detailed in Sect. 3.2).

Table 3 Trace metal species present in hydraulic fracturing flowback and produced water samples and current acute (and chronic) guideline concentrations for the protection of freshwater aquatic life according to Canadian Environmental Quality Guidelines (CEQ) and the US Environmental Protection Agency (USEPA)

					CEQ guidelines		USEPA guidelines	
Chemical	$\overline{X}$ conc.	Median conc.	Range	*N*	Acute	Chronic	Acute	Chronic
Antimony	0.25	0.1	0–9.9	71	ND	ND	ND	ND
Arsenic	0.37	0.077	0–26.1	93	ND	0.005	0.34	0.15
Barium	1,177.32	355	0–13,900	157	ND	ND	ND	ND
Beryllium	0.031	0.04	0–0.1	89	ND	ND	ND	ND
Cadmium	0.024	0.01	0–0.13	93	0.001	9.0×10^{-5}	0.0018	7.2×10^{-4}
Copper	0.21	0.071	0–4.15	125	ND	0.002–0.004[a]	ND	0.0065–0.034[a,b]
Iron (total)	203	46	0–18,432	163	ND	0.3	ND	1.0
Lead	0.11	0.03	0–3.48	118	ND	0.001–0.007[a]	0.082	0.0032[a]
Mercury	0.18	0.0002	0–14.6	83	ND	2.6×10^{-5}	0.0014	7.7×10^{-4}
Strontium	1,632.73	912	0.58–13,100	160	ND	ND	ND	ND
Thallium	2.34	0.1	0.0049–151	69	ND	8.0×10^{-4}	ND	ND
Zinc	8	0.1	0–685	128	0.037	0.007	0.12	0.12

ND No Data, *N* number of collective samples used to establish range. All values in mg/L

[a] Concentrations dependent on water hardness

[b] Concentrations based on a biotic ligand model analyses

2.3 Organic Chemicals

Similar to major ions, organic chemicals present in FPW are derived from two primary sources: from chemicals originally added to fracturing fluids for the purposes of inducing formation fractures and maintaining well viability but also from the formations themselves. Organic chemicals present in FPW samples derived from the formations being exploited are petrogenic in nature. As noted previously, certain drilling practices add specific organic chemicals to the fracturing fluid to aid extraction (e.g., biocides for antifouling properties and gelling agents such as ethylene glycols and differing petroleum distillates). Many of these fracturing fluid additives and their purposes can be found on the open-access website FracFocus.org. Although the majority of fracturing fluid organic additives are depleted during drilling operations, trace amounts of organic additives may still be present in collected FPW samples. However, much of the reported data on FPW does not include analysis of these organic additives. Thus, for the sake and purpose of this review, only organic chemicals originating from the formations that are present in FPW will be discussed.

The organic species present in FPW are both numerous and diverse. Although only organic chemicals that are common to most FPW samples are reported in Table 4, potentially thousands of organic chemical species may be present (He et al. 2017a). One of the more commonly measured organic chemicals in FPW are polycyclic aromatic hydrocarbons (PAHs), a class of organic compounds that have high toxicity, and which elicit negative impacts on both biota and ecosystems through many different mechanisms. This group encompasses both small organic chemicals, such as the double to 4-ring PAHs (e.g., naphthalene, phenanthrene, and pyrene), and relatively larger 5 to 10-ring PAH molecules (e.g., benzo[a]pyrene, perylene, and ovalene). It should be noted, however, that many larger PAH compounds ($\geq$6 rings) are often insoluble in water and sorb to organic carbon in aquatic systems (de Maag et al. 1998; Ma et al. 2010). Accordingly, such larger PAHs are immediately less bioavailable to aquatic organisms (although accumulation within sediments may become a toxicological concern).

2.4 Wellbore Reaction Products

One area of FPW chemical characterization which has recently begun to gain analytical attention is the presence of transformation products created during reactions involving the initial fracturing fluid compounds and the high-heat, high-pressure environments of a horizontally fractured wellbore. Albeit highly variable, and dependent on numerous factors including depth of formation, length of well, formation geology, etc., temperatures and pressures within a bore of a horizontally fractured well can reach up to ~200°C and 10,000 psi, respectively (Kahrilas et al. 2016; Nelson and Santus 2011; Shaffer et al. 2013). This creates