

Lawrence Berkeley National Laboratory

LBL Publications

Title

Flowback verses first-flush: new information on the geochemistry of produced water from mandatory reporting

Permalink

<https://escholarship.org/uc/item/5b52w5nb>

Journal

Environmental Science Processes & Impacts, 21(2)

ISSN

2050-7887

Authors

Stringfellow, William T

Camarillo, Mary Kay

Publication Date

2019-02-21

DOI



10.1039/c8em00351c

Peer reviewed



Cite this: DOI: 10.1039/c8em00351c

Flowback verses first-flush: new information on the geochemistry of produced water from mandatory reporting†

William T. Stringfellow *^{ab} and Mary Kay Camarillo ^{ab}

Unconventional oil and gas development uses the subsurface injection of large amounts of a variety of industrial chemicals, and there are concerns about the return of these chemical to the surface with water produced with oil and gas from stimulated wells. Produced water, including any flowback of injected fluids, must be managed so as to protect human health and the environment, and understanding the chemistry of produced water from stimulated wells is necessary to ensure the safe management of produced water. In 2014, California instituted mandatory reporting for all well stimulations, including sampling produced water two times and comprehensive chemical characterization of fluids injected and fluids recovered from stimulated wells. In this study, we analyzed data from mandatory reporting with the objective of closing previously identified data gaps concerning oil-field chemical practices and the nature of flowback and produced water from stimulated wells. It was found that the plug-flow conceptual model of flowback developed in shale formations, where salinity increases over time as produced water is extracted, was not appropriate for characterizing produced water from unconventional wells in these oil reservoirs, which are predominately diatomite and sandstones. In these formations stimulation caused a “first-flush” phenomena, where salts and metals were initially high and then decreased in concentration over time, as more produced water was extracted. Although widely applied to meet regulatory requirements, total carbohydrate measurement was not found to be a good chemical indicator of hydraulic fracturing flowback. Mandatory reporting closed data-gaps concerning chemical use, provided new information on acid treatments, and allowed more detailed analysis of hydraulic fracturing practices, including comparison of water use by geological formation.

Received 4th August 2018
Accepted 21st November 2018

DOI: 10.1039/c8em00351c

rsc.li/espi

Environmental significance

Mandatory reporting by industry allowed detailed analysis of hydraulic fracturing practices, including comparison of chemical use and produced water quality by geological formation. The pseudo-plug-flow conceptual model of flowback developed in shale formations, where salinity increases over time as produced water is extracted, was not applicable to unconventional wells in these oil reservoirs, which are predominately diatomite and sandstones. In these formations stimulation caused a “first-flush” phenomena, where salts and metals were initially high and then decreased in concentration over time, as more produced water was extracted. New information on acid treatments and the use of chemical indicators of flowback indicate that acid fracturing treatments are infrequently applied and the use of chemical indicators needs to be further validated.

1. Introduction

Hydraulic fracturing and other well stimulation techniques use significant volumes of freshwater and large masses of chemical additives.^{1–5} Well stimulation fluids are injected into

hydrocarbon bearing formations under pressure and, after the completion of the stimulation, fluid is pumped back out of the stimulated well, well clean-up may be performed, and the well is put into production.⁶ Although well stimulation typically occurs below the useable aquifer, there are concerns that return-flow of stimulation fluid (*i.e.* flowback) and produced water from stimulated wells may contain mixtures of added chemicals and reaction products that present unique and poorly understood risks during the management, treatment, and disposal of wastewater at the surface.⁷

Flowback is typically blended with and managed as produced water, which presents additional challenges to

^aEcological Engineering Research Program, School of Engineering & Computer Science, University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, USA

^bEarth & Environmental Sciences Area, Energy Geosciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA. E-mail: wstringfellow@lbl.gov; Tel: +1-510-486-7903

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8em00351c

insuring the safe management, reuse, and disposal of produced water. Hazards and risks associated with flowback and produced water include hazards associated with accidental spills, leaks, and other emissions.^{8–11} Concerns also arise from the potential contamination of surface water and aquifers due to poor well construction or maintenance, disposal of spent fluids, and disposal of fluids generated during oil and gas production.^{7,12,13}

Previous studies have investigated the phenomenon of flowback in produced water from stimulated wells and found that water quality of the return-flow changed over time, typically with an initial composition (as indicated by total dissolved solids (TDS) or other chemical indicators) similar to the injected fluid, with a gradual transition to more saline connate water.^{14–22} Combined, the results of these studies suggest that produced water from hydraulically fractured wells follows a non-ideal or pseudo plug-flow model, where the injected fluid comes out (flows-back) before the connate water is extracted. All of these studies were conducted in shales or tight-rock, except one that was conducted in a sandstone.¹⁵ In this paper, we examined flowback and produced water from diatomite and sandstone formations. Pseudo-plug-flow has become a common conceptual model of how flowback will behave, but how and when well stimulation chemicals and their degradation products “return” from the well with the produced water is an active area of research.

Several studies have taken a fundamental approach to characterizing the hazards and risks associated with well stimulation fluids by examining the chemical composition of the stimulation fluids injected into oil and gas wells. Most hazard analyses have focused on hydraulic fracturing, but some studies have also characterized chemical hazards associated with acid stimulation formulations.^{4,23,24} These studies identified persistent data gaps concerning which chemicals are used in well stimulation and their corresponding frequency of use, masses applied, and missing physical–chemical and toxicological information.^{3,25–27} Most of these studies have been limited by their dependence on information voluntarily disclosed by the oil and gas industry which prevents a definitive conclusion concerning well stimulation practices, since the completeness of the information is unknown.⁴ The reliance on voluntary disclosures has undermined public confidence in the safety of well stimulation, and stakeholders—the public, environmental groups, consumer advocates, scientists, and regulators—have sought more information and greater transparency concerning well stimulation practices.²⁸ This persistent lack of information has led some states and localities to limit or even ban hydraulic fracturing.²⁹

Oil and gas production is typically regulated on a state-by-state basis. In order to close data gaps, improve oversight, and respond to public concerns about the safety of hydraulic fracturing and other well stimulation activities, states are instituting new laws and regulations requiring mandatory reporting of a variety of information on well stimulation activities, most typically the location of stimulation treatments and chemical formulation of well stimulation fluids.^{30,31} In California, Senate Bill No. 4 – Well Stimulation: Oil and Gas (SB-4),

which went into effect in January 2014, was promulgated with the goal of providing greater transparency concerning well stimulation practices.³¹ In addition to mandating disclosure of well stimulation locations and formulations, SB-4 regulations also require water quality analysis of the water used for stimulation fluids (base-fluid), water quality analysis of produced water during the first three well-volumes of flow, and water quality analysis after 30 days of production.³² The timing of the sampling for water quality analysis was based on the plug-flow conceptual model, where the first sampling (within three well volumes) would characterize the injectate flowback and the second sampling (on or about 30 days after production) would represent the quality of the connate water that would be produced with oil over the life of the well. The SB-4 regulations include the requirement that the producer measure a chemical characteristic of the well stimulation fluid (indicator chemical) as part of the water quality characterization of the produced water.^{31,32} All but one hydraulic fracture included in this study applied guar gum as a gelling agent and used the measurement of total carbohydrates as a chemical indicator. Guar gum is used extensively as a gelling agent in hydraulic fracturing fluids both in California and nationally.^{4,5}

In this study, we analyzed the SB-4 mandated data concerning well stimulation chemistry and produced water quality from stimulated wells in California with the objective of determining the utility of this data in closing known data gaps concerning oil-field chemical practices and the nature of flowback and produced water from stimulated wells. These mandatory data, collected per SB-4 regulations, are compared with previous studies based on voluntary reporting to evaluate whether or not data gaps identified in previous studies are addressed. The majority of stimulations were performed in diatomite formations. Most stimulations were hydraulic fracture treatments, but some information is presented on acid fracturing, a practice that is less documented. Hydraulic fracturing practices are evaluated by geologic formation, producer, and service company. The SB-4 data includes water quality measurements made at two time points for almost 596 individual wells. Paired-data and pooled-data comparisons were made in the context of conceptual models and results from previous studies conducted in shale formations. We evaluated the use of total carbohydrates as an indicator compound and reviewed data for other constituents to identify other potential chemical indicators useful for differentiating injected fluid flowback from connate derived produced water.

2. Material and methods

2.1. Data sources

Well stimulation disclosure data, collected per SB-4 requirements,³² were obtained from the Division of Oil, Gas, and Geothermal Resources (DOGGR).³³ The disclosure data includes the dates of well stimulation, locations, chemicals used and masses, water volumes, base-fluid water quality, produced water quality, the production company producing the oil and gas (producer), and the supplier of stimulation chemicals and formulations (service company). The data set included water

quality results from two samples from each well. The first sample was collected within the first three wellbore volumes of flow, and the second sample was collected approximately 30 days after the start of production and the collection of the first sample.³² The disclosure data evaluated represents 618 well stimulations occurring at 596 wells between May 2015 and June 2016. There were 616 hydraulic fracturing treatments, one matrix acidizing treatment, and one acid fracturing treatment. The majority of wells (575) had only one stimulation treatment, although two or three stimulations were completed at other wells. All well stimulations took place in Kern County with the exception of one hydraulic fracturing treatment in Orange County.

Other sources of data included the state's oil and gas production database, which includes produced water volumes that were downloaded from the DOGGR website on February 6, 2017. Produced water volumes were used to estimate the volume of fluid recovered from wells at the time of the second sample. Volumes of fluid recovered at the time of the first sample were reported with the disclosure data. Other data used included well production start dates that were provided directly by the DOGGR on January 27, 2017. Where sample collection occurred prior to well production, a value of "0" was assigned to the days between the start of production and sample collection (for plotting). Rig release dates were provided by the DOGGR on February 17, 2017. Rig release is indicative of well age, as it occurs when oil and gas drilling and completion equipment and associated structures were last used at a well site.

Mandatory disclosure data were compared with voluntary disclosure data for chemicals used in hydraulic fracturing in California, as reported to the FracFocus registry, versions 1 and 2 (FF12), as summarized by Stringfellow *et al.*^{3,34} Mandatory data were also compared with data collected for chemical use in routine oil and gas production (well drilling, completion, and rework activities) in Southern California (Orange County and parts of Los Angeles, San Bernardino, and Riverside counties), as reported to the South Coast Air Quality Management District (SCAQMD) and summarized by Stringfellow *et al.*⁴

2.2. Geology

The majority of well stimulations occurred in the South Belridge oilfield (536 treatments), with additional stimulations being completed in Lost Hills (58 treatments), North Belridge (12), Elk Hills (5), McKittrick (4), North Coles Levee (2), and Brea-Olinda (1) oilfields (Table 1). South Belridge consists of a diatomite and brown shale formation that is of marine origin from the Miocene-Pliocene era.^{35–37} Well stimulation also occurred in Lost Hills, in the Etchegoin formation.³⁸ Other, less frequent well stimulation occurred in Antelope Shale and the McDonald and Stevens formations.³⁹

In California, formations are characterized by field-area-pool (FAP) codes, as described in California Code of Regulations (CCR) Title 14 Section 1760 and 1741[k]. Well fields and pool codes were disclosed by producers and area codes were determined from this information. When information was missing, a value of "00" was assigned to represent the "other" category.

Field, area, and pool codes were concatenated into a single string of numbers.

2.3. Masses and numbers of chemicals

All disclosed chemicals were identified according to Chemical Abstracts Services Registry Number (CASRN). Chemical masses were reported as percentages in each stimulation operation or, in some cases, in each stimulation stage. Water use was reported for each treatment, and not by stage. Where chemical use was reported by stage, it was assumed that an equivalent amount of water was used in each stage. Chemical masses were calculated using eqn (1). Where chemical use was reported by stage, the chemical masses used in each stage were summed.

$$\text{Chemical (kg)} = \frac{\text{water (barrels)}}{\text{no. stages in reporting}} \times 159 \frac{\text{L}}{\text{barrel}} \times \frac{1 \text{ kg water}}{\text{L}} \times \frac{\% \text{ chemical} \left(\frac{\text{kg chemical}}{\text{kg total}} \right)}{\% \text{ water} \left(\frac{\text{kg water}}{\text{kg total}} \right)} \quad (1)$$

Stimulation fluid density was calculated by dividing the total mass of additives by the reported stimulation fluid volume. Total dissolved solids (TDS) of stimulation fluids were calculated as the product of the chemical concentration (in ppm) and fluid density (in kg L⁻¹) plus the TDS of water used to formulate stimulation fluids.

In calculating the number of unique constituents per stimulation, multiple entries for a single constituent were pooled to avoid double-counting. Proppants were separated from carriers, assuming that proppants consisted of mineral solids (*e.g.* crystalline quartz) with mass concentrations greater than one percent.

2.4. Analysis software and methods

Disclosure data were evaluated using JMP version 13.0 (SAS Institute Inc., Cary, NC) and Grapher version 12 (Golden Software LLC, Golden, CO). Recovered water quality data were compared using the: (1) Wilcoxon signed rank test, a non-parametric paired *t*-test, where the *S* statistic was reported for *N* pairs and the probability was reported for a two-tailed test, and (2) Wilcoxon rank sum test, a non-parametric *t*-test, where the *S* statistic is also reported but for *N* observations and the probability was again reported for a two-tailed test (to indicate difference in either direction).

3. Results and discussion

3.1. Well stimulation treatments

All well stimulation treatments were hydraulic fracturing operations conducted using formulations containing guar gum (gel treatments), with the exception of one matrix acidizing treatment and one acid fracturing treatment (Table 1). The chemicals used for acid fracturing and matrix acidizing are identified in Table S-1.† Of the chemicals reported as used in matrix

Table 1 Median water and chemical use in well stimulation operations by different producers and service companies in California oil fields

FAP	Field	Pool	Stimulations	Median water intensity ^c (m ³ m ⁻¹)	Median chemicals (% mass)	Producer	Service company
0520020	South Belridge	Diatomite	486	1.35	0.63	A	A
			28	1.65	0.59	C	B
			21	1.78	0.31	A	B
4320027	Lost Hills	Etchegoin	35	4.46	0.23	B	C
			15	2.05	1.01	A	A
0500007	North Belridge	Diatomite	12	1.68	0.66	A	A
4320050	Lost Hills	Antelope/McDonald	8	2.94	3.01	A	A
4540610	McKittrick	Antelope Shale	4	4.68	1.92	B	C
2280015	Elk Hills	Upper (undifferentiated)	2	0.53	0.58	D	B
2280022	Elk Hills	Stevens (29R)	1 ^a	0.43	35.8	D	C
			1	7.22	0.66	D	B
1560025	North Coles Levee	Stevens (undifferentiated)	2	19.78	4.76	E	C
0700000	Brea-Olinda	No pool breakdown	1	2.94	0.35	C	B
2280024	Elk Hills	Stevens (31S)	1	13.11	1.10	D	B
0520000	South Belridge	No pool breakdown	1 ^b	1.22	13.5	A	A

^a Matrix acidizing treatment. ^b Acid fracturing treatment. ^c Volume of water used per length of well stimulation zone.

acidizing and acid fracturing, seventeen chemicals had not been reported previously under voluntary reporting requirements.^{3,4,34} There is limited published information on acid treatments, including matrix acidizing and acid fracturing,^{4,23,40–42} and the SB-4 regulations are helping close the data gap concerning acid treatments identified in previous studies concerning chemical use and frequency of application in California.^{6,7}

A complete list of the chemicals used for well stimulation on California between May 2015 and June 2016 is given in Table S-1.† There were 54 stimulation chemicals identified *via* mandatory reporting under SB-4 that had not been identified in previous studies.^{3,4,34} The newly identified chemicals were used infrequently (in less than 10% of well stimulations), except the clay control agent hydroxytrimethylene bis(trimethylammonium) dichloride (55636-09-4), which was used in 84% of treatments (522 treatments). Previously in California, as revealed by voluntary reporting, a different clay control agent, 1,2-ethanediaminium, *N*1,*N*2-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-*N*1,*N*2-bis(2-hydroxyethyl)-*N*1,*N*2-dimethyl-, chloride (1 : 4) (138879-94-4), was used most frequently (66% of all treatments).^{3,34} The reason for this change in clay-control strategy is not known and may be inconsequential from a risk management perspective, but in the absence of publicly available information on the toxicity, biodegradability, or other environmentally critical properties of clay control agents, it may be premature to dismiss risk from these materials altogether.^{3–5,43}

Twenty of the newly identified chemicals were chlorinated, brominated, or iodated aromatic hydrocarbons (Table S-1†). Halogenated aromatic compounds can be environmentally persistent and toxic, so there is specific interest in the use of these types of compounds in the context of produced water reuse and risk assessment.³ While environmentally persistent, these compounds appear to have been used as tracers and tracer-tests were only conducted in eight well stimulations, suggesting use of these chemicals is not routine. The

halogenated hydrocarbons were used in approximately 1% of all treatments and at doses of <1 kg per treatment. To our knowledge, this is the first time the use of these chemicals has been acknowledged in California, illustrating the value of mandatory reporting for evaluating the hazards and risks associated with well stimulation and other oil-field practices.

There were variations in the composition of gel-treatment formulations depending on the producer-service company combination and the formation being treated (Table 2). Anecdotal evidence presented in Fig. 1 suggests the source of water being used as the base-fluid may also influence stimulation fluid formulation. Service companies were somewhat consistent in their use of chemicals within the same geological formation (Table 2). The coefficient of variation (CV) for number of chemicals used per stimulation within a FAP was less than 20% and the CV of concentrations of chemicals as indicated by salinity (as TDS), guar, and boron were less than 20%, with the exception one case when the salinity of the fracturing fluids demonstrated a CV of 33% (Table 2). When all hydraulic fracturing stimulations ($N = 616$) are considered, the chemical properties showed a greater variation: the CV for salinity as mg L⁻¹ TDS was 58% (9000 mean ± 5300 standard deviation); guar gum was 24% (2500 ± 600 mg L⁻¹); and boron CV was 36% (50 ± 18 mg L⁻¹).

Other less quantifiable information also suggests some predictability in stimulation fluid composition. For example, one service company consistently used the combination of 5-chloro-2-methyl-3(2*H*)-isothiazolone (26172-55-4) and 2-methyl-3(2*H*)-isothiazolone (2682-20-4) as a biocide, while another service company operating in the same FAP used tetrakis hydroxymethyl phosphonium sulfate (55566-30-8), 1,2-benzisothiazolin-3-one (2634-33-5), and tetrahydro-3,5-dimethyl-1,3,5-thiadiazine-2-thione (533-74-4). Additionally, companies have proprietary chemicals, such as clay control agents, that may not be available to competitors.⁵

Evaluation of chemical use by geological formation and company helps explain the seemingly large number of

Table 2 Analysis of hydraulic fracturing fluid composition by geologic formation (field-area-pool, FAP) and producer-service company combination for formations with sufficient well stimulations for analysis ($N \geq 15$). Results indicate that there is a subset of chemicals used in different formations and that all chemicals are not used in all areas. Hydraulic fracturing fluid formulations, as indicated by parameters such as total dissolved solids (TDS), guar gum, and boron concentrations, appear to be different between geologies and operators, but consistent within a FAP for a given operator

FAP	Producer/service company	Well stimulations (N)	Chemicals used per stimulation ^{a,b}	Total individual chemicals used in FAP by producer and service company ^c	TDS ^a (mg L^{-1})	Guar gum ^a (mg L^{-1})	Boron ^a (mg L^{-1})
0520020	A/A	487	22 ± 2	46	8000 ± 2000	2500 ± 500	50 ± 8
0520020	C/B	28	21 ± 5	26	$16\,000 \pm 1000$	2600 ± 300	100 ± 8
0520020	A/B	20	12 ± 0^d	13	4300 ± 500	1800 ± 500	30 ± 4
4320027	B/C	35	13 ± 2	35	6500 ± 400	1600 ± 200	30 ± 4
4320027	A/A	15	23 ± 1	30	$12\,000 \pm 4000$	2700 ± 300	50 ± 9

^a Mean \pm standard deviation. ^b Excluding base fluid and proppant. ^c Total number of individual constituents reported in the study period was 178 (including chemicals, proppants, and water). ^d All stimulations used 12 chemicals each.

chemicals used in hydraulic fracturing.^{25,44,45} The formulations varied between formations, but within an individual FAP service companies appeared to adhere to a consistent approach, adding an element of predictability to hydraulic fracturing practices that should be welcome news for regulators. There may be many different reasons for treatments to differ widely, even within the same geological zone, including geological heterogeneity, well depth, economic decisions, intellectual property, and operational preferences, but these results suggest that there is a consistency to on-field practices that serves to increase the predictability or reliability of risk assessment efforts.

3.2. Water use for well stimulation

As the result of new reporting requirements under SB-4 regulation, information is now available on the quality of waters used as base-fluid for well stimulation formulations (Table 3). The predominant source of water for fluid formulation is surface water from the California Aqueduct, which is appropriate for other beneficial uses, as indicated by salinity between $150\text{--}540 \text{ mg L}^{-1}$ TDS (Table 3). In addition to fresh surface water, there was some use of brackish groundwater ($4400\text{--}6400 \text{ mg L}^{-1}$ TDS) and recycled produced water ($10\,000\text{--}38\,000 \text{ mg L}^{-1}$ TDS) for fluid formulation, although use of alternative water supplies was not common. The California Aqueduct is a major source of fresh water for California, which puts water use for well stimulation in direct competition with demand by urban and agricultural uses, however, the total quantity of water used in all well stimulations during the studied period was approximately $230\,000 \text{ m}^3$, which is a small fraction of the aqueduct capacity and the estimated 13 trillion m^3 annual surface water use in California.^{46,47} Requiring characterization of the water quality of the water used as a bulk-fluid for formulation closes an important data gap identified in previous studies⁶ and is useful for understanding the phenomena of flowback in the context of produced water.

The volume of water used was a function of stimulation zone length, but also varied by the reservoir geological properties as indicated by FAP code (Fig. 2). Overall, the mean (\pm standard deviation) and median volume of water used was $421\text{+/-}334 \text{ m}^3$ and 381 m^3 per stimulation, respectively, which is consistent

with estimates made in previous studies concerning California oil fields and less than the average water use of 9200 m^3 per treatment in the U.S. overall.^{34,48} The intensity of water use (volume of water per length of stimulation zone) was largely consistent within oil fields independent of operator or service company (Table 1), with water intensity being higher in the Lost Hills field ($3.8 \pm 1.38 \text{ m}^3 \text{ m}^{-1}$) than North Belridge ($1.68 \pm 0.10 \text{ m}^3 \text{ m}^{-1}$) or South Belridge ($1.59 \pm 0.87 \text{ m}^3 \text{ m}^{-1}$).

Mandatory reporting offered a unique opportunity to compare water use intensity between companies operating in the same FAP (Table 1). In the same FAP (4320027), one company had a water use intensity more than twice that of another company (Table 1, $2.1 \pm 0.14 \text{ m}^3 \text{ m}^{-1}$ versus $4.5 \pm 0.82 \text{ m}^3 \text{ m}^{-1}$). The two service companies also used different chemical formulations (Fig. 1 and Table 2), with the treatments with greater water intensity using less chemicals in this case. Comparison of different practices within the same FAP (Fig. 1) suggests that there are opportunities for companies to modify hydraulic fracturing practices to improve water conservation and, perhaps, utilize green-chemistry alternatives.

3.3. Temporal characterization of produced water chemistry in context of a plug-flow model

The most common conceptual model for produced water extracted from hydraulically fractured wells is the pseudo-plug-flow model, where the initial flush of water from the well will be a flowback of injected fluid followed by a transition to connate water from the formation. A characteristic of this model is that samples collected at early time points are expected to be at lower concentration than samples collected at later time points, until a maximum concentration is reached (*e.g.*^{49,50}). The SB-4 requirement for sampling at the initial flow from the well and then again after the well has been produced for a month is based on this model.^{7,32} We compared the water quality of the initial sampling and the final sampling taken from the same well to test the hypothesis that the initial flow will consist of well stimulation fluid flowback. This analysis was conducted for the three oil fields (South Belridge, North Belridge, and Lost Hills) which sufficient replicate data was available (Table 1).

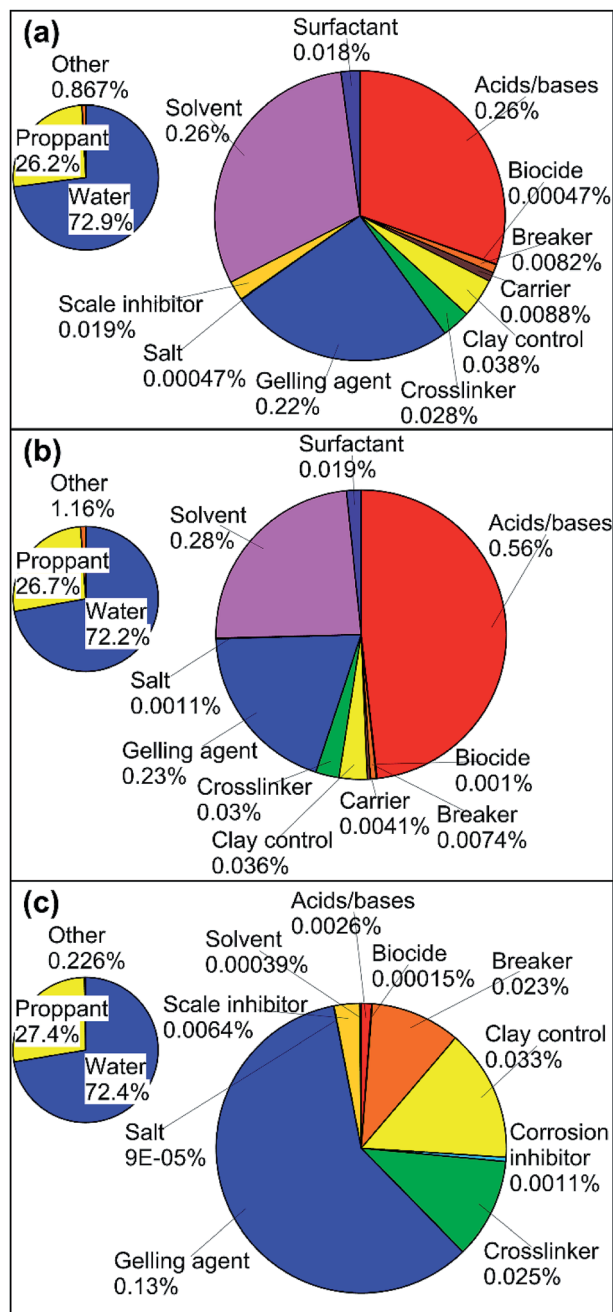


Fig. 1 Relative mass fraction of total chemicals used (pie chart) and mean mass concentration (%) for hydraulic fracturing treatments conducted in the same geologic formation in the Lost Hills field (FAP 4320027). Formulations varied by several factors: (a) service company A using California Aqueduct water ($N = 13$; TDS = 520 mg L⁻¹); (b) service company A using produced water ($N = 2$; TDS = 6600 mg L⁻¹); and (c) service company C using produced water ($N = 35$; TDS = 4400 mg L⁻¹). Chemical additives were pooled by function according to Stringfellow *et al.* (2017).

Table 4 compares initial and final water quality for samples taken at approximately three well volumes and after thirty days as required by SB-4 well stimulation regulations.³² In contrast to what would be expected from the pseudo-plug-flow flowback model, for most constituents the concentration measured in the initial sample was higher than the final concentration (Table 4).

For example, the mean TDS was 70 000 mg L⁻¹ for the initial samples and declined to less than 26 000 mg L⁻¹ in later samples (Table 4 and Fig. 3). In comparison, the salinity of the injected fluid is approximately 9000 mg L⁻¹ TDS, suggesting the injectate flowback has little direct influence on the initial produced water quality. The mean recovered flow at the initial sampling was 54 ± 157 m³, which represents 16% of the injected fluid volume, and the final sample was taken at 815 ± 521 m³, which is equivalent to 228% of the injected volume.

Many constituents were significantly higher in the first sample than the second, as determined by paired *t*-test of initial and final samples from the same well (Table 4). Ions, such as chloride, calcium, potassium, magnesium, and sodium, and metals, including copper, iron, and zinc, were higher in the initial sample than the final sample. Radioactive materials, including radium (Ra-226 and Ra-222), beta-counts, and alpha-counts, were also higher in the initial samples than the final samples (Table 4). This result is notable because the radioactivity of surface waters used in most fluid formulations was low (Table 3), which clearly demonstrates that radioactive materials found in higher concentrations in the initial sample are derived from material extracted from the reservoir geology, rather than representing a signal of flowback of the injected fluid.

The stimulation fluids are likely mobilizing sorbed inorganic chemicals, including radioactive materials, from within the formation,^{51,52} however, it should be noted that the highest Ra-226 value observed in this produced water, 917 pCi L⁻¹, was an order of magnitude lower than that observed in gas wells.^{14,16,21,22} As an example, Barbot *et al.*¹⁴ measured Ra-226 as high as 9280 pCi L⁻¹ in Northeastern Pennsylvania.

From this analysis we propose a “first-flush” model, where hydraulic fracturing disturbs the formation and extracts minerals from reservoir rocks, which are then brought to the surface with produced water. First flush phenomena are common in other environmental process, including storm-water drainage, where sudden inputs of fluid and energy disrupt system equilibrium (*e.g.*⁵³). A characteristic of this model is that earlier samples may be of higher concentration than later samples. The model of flowback returning as a pseudo-plug-flow is not applicable to these oil reservoirs (Table 1) and perhaps not to reservoirs of migrated oil in general, which tend to contain more water than source-rock. Prior studies that observed pseudo-plug-flow flowback were conducted in shale and “tight-rock” formations and examined gas or shale-oil production from source-rock,^{14,16–22} whereas this study examined production of migrated oil from diatomite and sandstone (Table 1). There is some evidence that a first-flush phenomena can occur in shales, indicated by higher initial concentrations of various constituents or an increase to a peak concentration followed by a decline to a steady concentration, presumably representative of the connate water.^{17,20,54}

3.4. Temporal analysis of changes in produced water salinity

Temporal analysis suggests that the first-flush is not a long-lived phenomenon. As expected, sample collection times in relation to the start of production showed a natural variance, which was

Table 3 Summary of water quality of base-fluid used to formulate well stimulation fluids. Radioactive data are only shown where the results are above the reported detection limit (RDL)

Constituent	California Aqueduct					Elk Hills PW	LOK W1	T600	Tulare PW	Tulare water ^b	Well water ^c	West Kern
	01/12/15 ^a	10/15/15	11/12/15	12/02/15	04/29/16	11/12/15	8/26/15	11/13/15	01/06/16	08/11/15	07/19/16	05/01/15
	Alkalinity, mg L ⁻¹ as CaCO ₃	44	56	79	62	91	270	126	830	1000	70	620
Alpha, pCi L ⁻¹	1.66	<RDL	7.98	<RDL	2.74	<RDL	—	34.2	<RDL	<RDL	<RDL	14.9
Beta, pCi L ⁻¹	—	<RDL	3.72	<RDL	2.59	<RDL	—	—	<RDL	<RDL	29.6	<RDL
Boron, mg L ⁻¹	0.2	0.15	0.18	0.12	0.32	23	0.002	36	45	3.6	7.55	0.29
Radium-226, pCi L ⁻¹	0.78	<RDL	<RDL	2.05	<RDL	<RDL	—	9.13	<RDL	3.29	<RDL	<RDL
Radium-228, pCi L ⁻¹	<RDL	—	—	—	—	—	—	10.1	—	1.39	1.10	<RDL
Radon, pCi L ⁻¹	—	—	<RDL	<RDL	—	<RDL	—	—	<RDL	—	—	—
Radon-222, pCi L ⁻¹	—	<RDL	—	—	<RDL	—	—	50.8	—	96	—	—
TDS, mg L ⁻¹	520	540	320	150	390	38 000	—	14 000	10 000	4400	6400	320
Uranium, pCi L ⁻¹	<RDL	—	—	—	—	—	—	—	—	—	<RDL	12
Uranium, µg L ⁻¹	—	—	—	—	—	—	—	—	—	—	—	18

^a Water used in Lost Hills (FAP 4320027) by producer A ($N = 13$). ^b Water used in Lost Hills (FAP 4320027) by producer B ($N = 35$). ^c Water used in Lost Hills (FAP 4320027) by producer A ($N = 2$).

used to further investigate the changes in water quality over time. Data were analyzed by geological formation (FAP) and changes in water quality were evaluated as a function of time from when the well was put into production (Fig. 3). The majority of hydraulic fracturing stimulations occurred in the South Belridge oilfield FAP 0520020 and these data are presented in Fig. 3.

In Fig. 3, the temporal changes in the TDS of produced water from South Belridge can be seen in detail. The produced water TDS was initially as high as 900 000 mg L⁻¹ and then declined over time, trending toward an equilibrium concentration of about 10 000 to 40 000 mg L⁻¹. There is a large variability in the initial TDS concentration and in some cases the salinity of the first sample is sometimes low, which could indicate flowback of hydraulic fracturing fluids formulated with freshwater, but could also indicate the presence of acids or other solutions (also formulated in freshwater) which are used as the well is put into production. Since well cleaning fluids are not injected into the formation under pressure, these fluids are not technically part of a well stimulation treatment and is not required to be documented under SB-4 regulations.^{4,6,32}

The temporal pattern for TDS observed here with formations containing migrated oil is different from what has been reported for source-rock undergoing hydraulic fracturing.^{14,17,21,22,49,54} In prior studies, the TDS is typically low initially and increases as water production continues. The initial increase in TDS can be rapid, indicating a short period of initial flowback that typically occurs over the first few weeks of production.^{14,17,22,49,54} The rate at which TDS increases can also be more gradual, occurring over more than one year following the start of production.²¹ However, it has been observed that in some cases the TDS can peak and then start to decline.^{17,20,54}

In this study, the trend is for the initial flow to be higher in salinity followed by a transition over a period of days toward less

variation and a lower salinity, presumably more representative of the formation fluid. Both paired and grouped *t*-tests (alpha = 0.05) show that injected fluids are significantly less concentrated in salts and boron than either the first sample or the final sample. Fig. 4 shows a comparison of the injectate fluid salinity to the salinity of the first and final samples for FAP 0520020, where the most samples were collected. The statistical analysis supports the temporal analysis by field (Fig. 3) and is consistent with the results of paired analysis for these stimulated wells (Table 4). The collection of only two samples per well does not allow modeling of individual wells, but all of the statistical and graphic analysis supports the conclusion that flowback and pseudo-first order flows are not being observed in these formations, and that a first-flush conceptual model is more appropriate in the context of produced water management from these wells.

3.5. Indicators of stimulation fluids in produced water

Regulations governing well stimulation in California require that, as part of their water quality monitoring program, producers select and measure a chemical component characteristic of their well stimulation fluid in produced water from stimulated wells.³² The purpose of this measurement is to help characterize flowback and identify well stimulation chemicals in produced water over time. In most cases, operators measured total carbohydrates as an indicator of hydraulic fracturing fluid in produced water. Total carbohydrates was intended to measure residual gelling agents originating from stimulation fluids since guar gum is used extensively in hydraulic fracturing.^{5,15} Guar gum was used in 617 of the 618 well stimulation treatments (Table S-1†), with a mean concentration of 2500 ± 600 mg L⁻¹ in the stimulation fluid. However, the use of the total carbohydrate as an indicator has not been validated and

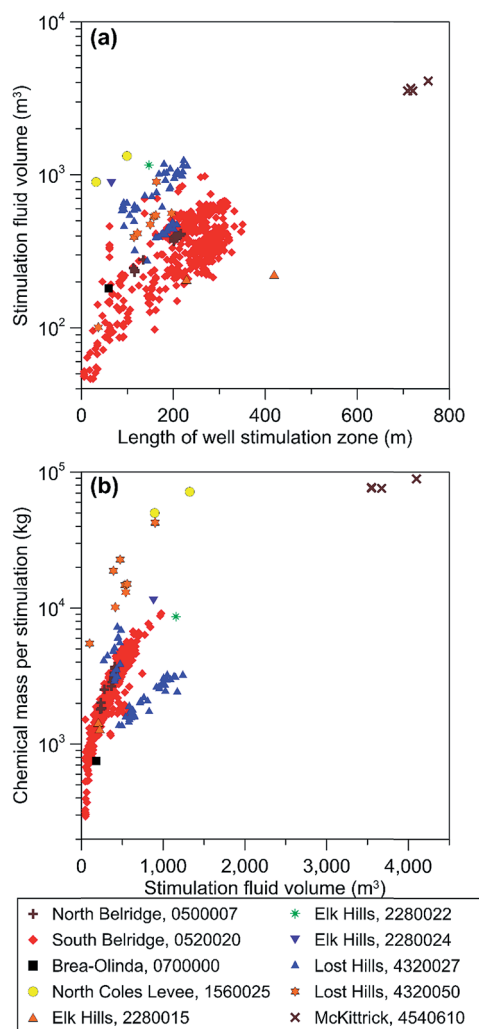


Fig. 2 Relationship between: (a) hydraulic fracturing stimulation fluid volume and zone length, and (b) between chemical masses added to hydraulic fracturing stimulation fluid (excludes water and proppants) and fluid volume. Data are grouped by field-area-pool (FAP) code ($N = 616$).

there is not a standard or approved method for carbohydrate measurement in produced water.

In order to investigate the utility of measuring carbohydrate as an indicator chemical, a paired t -test was performed between initial and final water quality results for individual wells. This analysis indicated that measurement for total carbohydrate concentration did not change over time. The mean total carbohydrate concentration was $187 \pm 156 \text{ mg L}^{-1}$ in the initial sample versus $188 \text{ mg L}^{-1} \pm 173 \text{ mg L}^{-1}$ for the last sample from the same well. A temporal analysis of carbohydrate concentration over time was conducted and this analysis also indicated total carbohydrate did not change over time (Fig. 3). This result is unexpected. After stimulation, guar gum is dissolved with breaker chemicals (typically enzymes) for the expressed purpose of releasing the guar from the formation, so it was expected that initial guar concentrations would be high and decline over time. Additionally, most other constituents did not show a steady or constant concentration between first and second samples or over time (Table 4 and Fig. 3).

The results of this analysis indicate that either (a) guar is returning at a consistent rate of approximately 180 mg L^{-1} for the duration of the sampling period; or (b) the carbohydrate method is subject to interference and is giving a false positive measurement for carbohydrate; or (c) that there is another sources of carbohydrate than guar gum in oil reservoirs. It seems unlikely to the authors, given the biodegradability of guar gum and the variability of the other water quality parameters, that there is a consistent flow of 180 mg L^{-1} guar from the well over time. The more likely interpretation of the result is that there is an interference that gives a false positive result for carbohydrates or that there is another source of carbohydrates in produced water.

Recent studies in our laboratory have shown that produced water from wells that were not hydraulically fractured can also be positive for carbohydrate by the anthrone and phenol methods (data not shown). Previous studies have shown that aldehydes and other chemicals can interfere with the carbohydrate test (e.g.⁵⁵). Studies are on-going to determine if there is a chemical interference or if there may be another source of carbohydrates in produced water. One hypothesis being investigated is that bacteria may be a source of carbohydrates in produced water.

Total carbohydrate analysis is not yet a State certified or standard method and current analysis may have insufficient quality control. Further studies are being conducted to establish standard protocols for the carbohydrate analysis in the context of water quality monitoring, to determine the applicability of the analysis to produced waters, and to develop methods for the measurement of alternative and perhaps more appropriate indicator compounds in produced water.

3.6. Other water quality parameters as indicators of injected fluid flowback

We investigated if other measurements indicated that injected fluids were flowing back with produced water. Of all the parameters measured only five other constituents or parameters (alkalinity, boron, bromium, hydrogen sulfide, and pH) showed a significant increase between first and last sample events (Table 4). Of these parameters, alkalinity and boron were considered further as indicators of hydraulic fracturing fluid flowback.

Although alkalinity is not a specific parameter for well stimulation fluid, alkalinity gave the strongest signal indicative of a flowback type phenomena of all the water quality parameters measured, in that the alkalinity in produced water tended to increase over time (Fig. 3). In the initial samples in South Belridge FAP 0520020, the alkalinity was variable and frequently low, even less than 100 mg L^{-1} as CaCO_3 and within two days after the start of production, the alkalinity was higher, typically $1000\text{--}5000 \text{ mg L}^{-1}$ as CaCO_3 (Fig. 3). By the 30 day period the produced water shows a stable alkalinity of 1000 to 5000 mg L^{-1} as CaCO_3 and appears to be representative of formation fluids.

The alkalinity of the stimulation fluids were not reported, but some information about injectate alkalinity is known. Water used in formulating stimulation fluids had moderate to

Table 4 Comparison of initial and final water quality for samples taken at approximately three well volumes and after thirty days as required by SB-4 well stimulation regulations. This analysis was conducted for the three oil fields (South Belridge, North Belridge, and Lost Hills) which sufficient replicate data was available (Table 1). Statistical significance is reported for *t*-test on paired data from the same well. Measured samples below the reported level of detection were assigned a value of zero for this analysis

Analyte	<i>N</i> initial	Mean initial	SD initial	<i>N</i> final	Mean final	SD final	Paired statistical different 1 = yes 0 = no	% Change	Final < initial = 1 increase = 0 no change = 2
Alk (CaCO ₃)	440	2000	1000	441	2900	700	1	32	0
Alpha	472	100	300	476	50	70	1	-53	1
B	475	90	30	476	100	20	1	13	0
Ba	475	8	5	476	8	5	0	4	2
Be	475	0.001	0.005	476	0.0001	0.001	1	-79	1
Beta	472	600	2000	476	200	400	1	-65	1
Br	475	110	60	476	120	40	1	14	0
Ca	475	7000	20 000	476	300	200	1	-96	1
Cd	475	0.00002	0.0005	476	0 ^a	0	0	-100	2
Cl	475	30 000	50 000	476	14 000	3000	1	-50	1
Co	475	0.003	0.007	476	0.0002	0.002	1	-74	1
Cr	475	0.02	0.06	476	0.02	0.06	0	41	0
Cr(vi)	440	0.004	0.03	441	0.0006	0.003	1	-83	1
Cu	475	0.1	0.4	476	0.01	0.03	1	-85	1
F	475	1	4	476	0.1	0.8	1	-94	1
Fe	475	40	60	476	20	40	1	-35	1
H ₂ S	467	0.05	0.3	476	0.1	0.6	1	114	0
K	475	900	3000	476	200	100	1	-72	1
Li	475	30	60	476	7	3	1	-72	1
Mg	475	500	1000	476	100	50	1	-71	1
Mn	475	2	5	476	0.5	0.5	1	-76	1
Mo	475	0.003	0.02	476	0.004	0.02	0	49	2
Na	475	9000	8000	476	9000	2000	0	3	2
Ni	475	0.03	0.2	476	0.03	0.1	0	-26	2
Pb	475	0.03	0.2	476	0.001	0.01	1	-95	1
pH	432	7.4	0.6	441	7.7	0.2	1	4	0
Ra-226	471	60	100	476	20	10	1	-59	1
Rn-222	441	1000	10 000	449	300	2000	0	-77	2
Sb	475	0.01	0.08	476	0.01	0.06	0	-17	2
Se	475	0.2	0.9	476	0.1	0.2	1	-74	1
SO ₄	475	90	600	476	30	100	1	-70	1
Sr	475	100	400	476	10	6	1	-92	1
TDS	475	70 000	100 000	476	26 000	6000	1	-61	1
V	475	0.01	0.05	476	0.004	0.05	0	1	2
Zn	475	0.3	1	476	0.1	0.3	1	-76	1

^a All measurements were below limit of detection.

low alkalinity (<1000 mg L⁻¹ as CaCO₃). The most frequently used base fluid was surface water which had an alkalinity of 44–91 mg L⁻¹ as CaCO₃ (Table 3). Although the hydraulic fracturing fluids can contain a variety of acids, including oleic acid, boric acid, phosphonic acid, acetic acid, and citric acid, acids were only added in 20% of the applications, with the exception of phosphonic acid which was added to 67% of the treatments. Phosphonic acid is a corrosion and scale inhibitor and carboxylic acids are frequently added to hydraulic fracturing fluids as chelating agents for scale and iron control rather than pH adjustment.³ In fact, bases were used more frequently in stimulation fluids than acids, with sodium hydroxide (1310-73-2) being used in 519 out of 616 hydraulic fracturing treatments (84%). Given the infrequent use of acids and the frequent use of bases, it seems unlikely that the initial low alkalinity is the result of the stimulation fluids and is more likely a signal from

acidic well-cleaning solutions. Since acids and potentially other cleaning solutions are used on both stimulated (unconventional) and conventional wells,⁴ future studies should consider comparing water quality between conventional and unconventional sources of produced water.

Alkalinity is a poor indicator in the context of indicating injected fluid return-flow because of the lack of specificity of the measurement, but changes in alkalinity have been used to indicate flowback in previous studies. In studies of unconventional gas wells, alkalinity has been shown to decrease over time,^{14,21} or to first increase to a peak and decrease,⁴⁹ but changes in alkalinity can result from biological or chemical transformations, including mineral dissolution or precipitation within the formation.^{14,54} The alkalinity measurements in produced water also need to be interpreted with caution because produced waters can contain high concentrations of

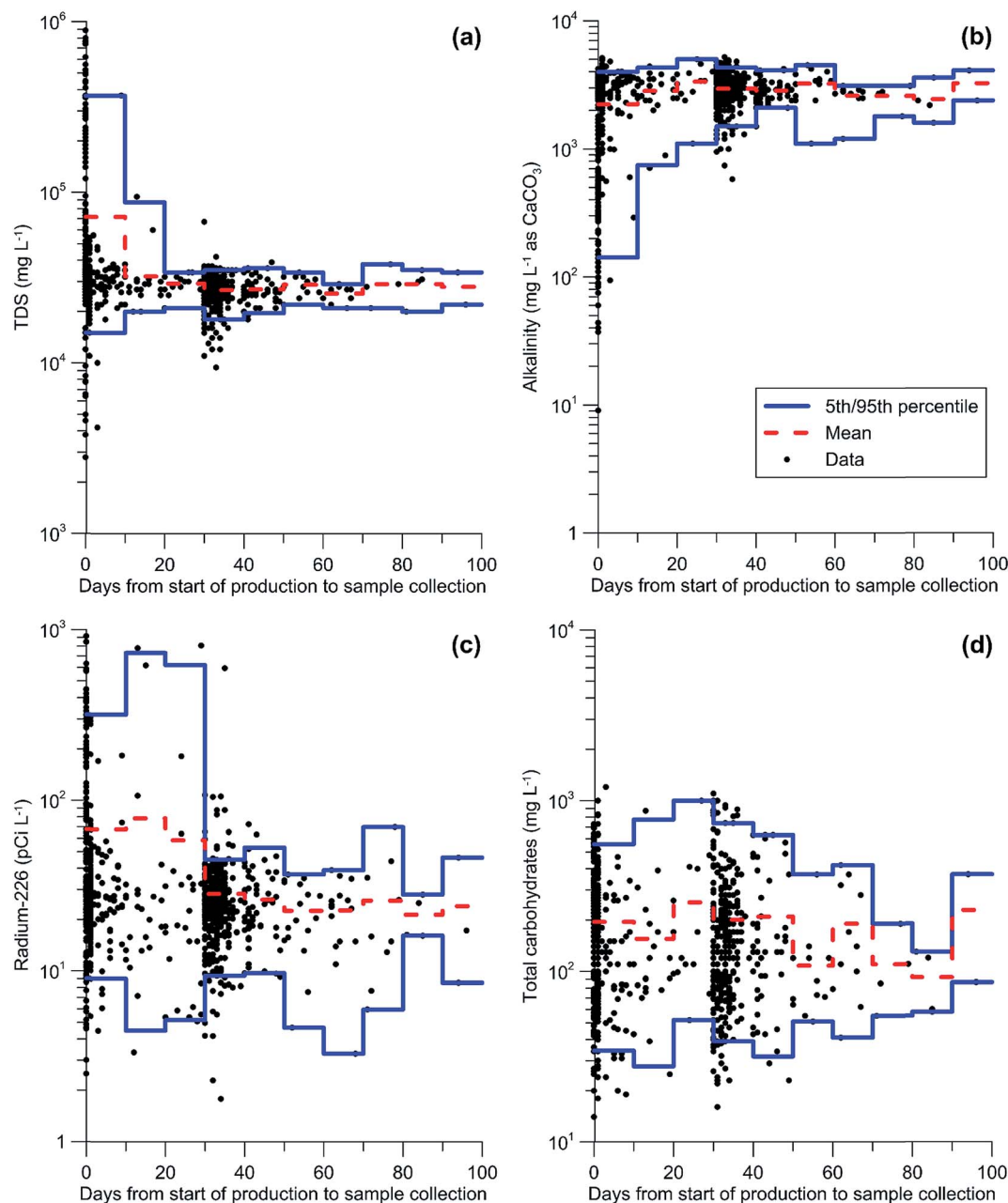


Fig. 3 Recovered fluid water quality following hydraulic fracturing in the South Belridge field (FAP 0520020) with data shown for: (a) total dissolved solids (TDS), (b) alkalinity, (c) radium-226, and (d) total carbohydrates. Only radium-226 concentrations that were above the reported detection limit were included in the plot and analysis.

acetic acid or other similar carboxylic acids, that have pK_a values near the total alkalinity end point (~ 4.5) and can interfere with measurements of alkalinity.⁵⁶

3.7. Boron as an indicator of injected fluid flowback

Boron is a common ingredient in gel treatment formulations, so the use of boron as an indicator compound of stimulation fluid flowback deserves some consideration. All of the hydraulic fracturing treatments contained boron, with an average concentration of $50 \pm 18 \text{ mg L}^{-1}$. Boron was added to hydraulic fracturing fluids in a number of forms, including boric acid

(10043-35-3), methyl borate (121-43-7), sodium tetraborate decahydrate (1303-96-4), and monoethanolamine borate (26038-87-9) (Table S-1†). Additionally, in a few cases, the bulk-fluid also contained significant concentrations of boron (Table 3).

Boron concentration increased from an initial concentration of $\sim 90 \text{ mg L}^{-1}$ at 3 well volumes to $\sim 100 \text{ mg L}^{-1}$ after a month of well production (Table 4). Paired *t*-test analysis of first and last samples from individual wells indicate that this difference is significant (Table 4). Although it is possible that boron concentration was lower in initial produced water samples due

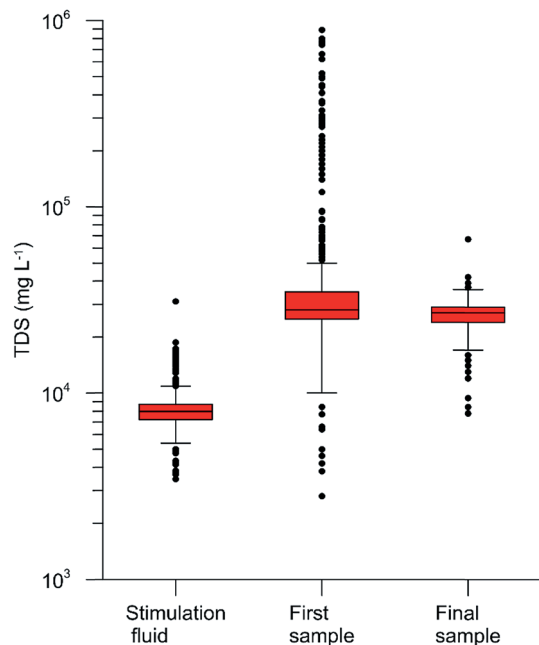


Fig. 4 Comparison of total dissolved solids (TDS) calculated in the stimulation fluid and measured in the first and final samples recovered from wells undergoing hydraulic fracturing in the South Belridge field (FAP 0520020). The salinity of the injected fluid is significantly less than the salinity of either the first or last samples by both paired and grouped *t*-tests ($\alpha \leq 0.05$). The boxplot whiskers are extended to the outermost points that are within 1.5 of the interquartile range.

to dilution of connate water with flowback, the results are far from conclusive. Diluent effects could also occur from the use of well clean-out solutions. The sampling results do show that produced waters contain significant concentrations of boron, which could impact their value for reuse, either on-field or for agriculture.

4. Conclusions

Mandatory reporting under SB-4 regulations³² has served to close data gaps concerning unconventional oil and gas development, which improves regulatory oversight, and should serve to increase public confidence.²⁸ Acid stimulation treatments, including matrix acidizing and acid fracturing, are now reported statewide for the first time and were found to be infrequently applied. Mandatory reporting of chemical-use mostly validated the findings of previous studies reliant on voluntary reporting, however the types of clay control agents used appears to have changed, and there is a greater diversity of biocides being used than previously understood.^{3,5,7} To our knowledge, this is the first time that halogenated aromatic compounds have been identified as additives to hydraulic fracturing fluids in California, although previous studies have reported halogenated reaction products in flowback and wastewaters from oil and gas extraction.^{57–59}

Chemical use and water use was found to vary with factors such as the geological reservoir (as identified by FAP) and the companies conducting the stimulation treatment. Although

water use intensity varied by reservoir geology, large differences in water use were observed between practitioners in the same geological deposit. In some cases, produced water was recycled for use in hydraulic fracturing and there was evidence of flexibility concerning chemicals used for any individual treatment. These observations suggest that there are opportunities for water conservation and green chemistry, however water use for well stimulation in California is a small fraction of water demand in the state.

Hydraulically fractured wells exhibited a “first-flush” phenomena where TDS, individual ions (*e.g.* chloride, calcium, potassium, magnesium, sodium), and metals, (copper, iron, and zinc), were higher in the initial sample than the final sample. Radioactive materials, including radium, beta-counts, and alpha-counts, were also higher in produced water initially and declined over time. This result is in contrast to previous studies that found the salinity of the produced water from stimulated wells typically increased over time, fitting a conceptual model for. Pseudo-plug-flow, where the injected fluid returns before significant connate water is produced.^{14–22}

The difference in the observation of first-flush *versus* pseudo-plug-flow can be explained at least in part by differences in geology. Previous studies have mostly characterized produced water and flowback phenomena in hydraulically fractured source-rock: shales or tight-rock.^{14,16–22} Many of these studies occurred in gas fields, which typically produce less connate water than oil fields. In contrast, this study investigated produced water and flowback phenomena in migrated oil reservoirs (not source-rock) located in diatomite, sandstone, and carbonate formations (Table 1). The model of flowback returning as a pseudo-plug-flow is not applicable to these oil reservoirs and perhaps not to reservoirs of migrated oil in general, which are less dense than source-rock and tend to produce more water than gas fields.

Operators are required to measure a major chemical used to formulate the well stimulation fluid as an indicator of hydraulic fracturing fluid in produced water.³² All operators using gel treatments chose total carbohydrate as an indicator chemical, since guar gum is used extensively in hydraulic fracturing.^{5,15} Measurement of total carbohydrate in produced water apparently yielded a false positive result for guar. Total carbohydrate analysis is not a state certified or standard method and it hypothesized that the measurement of guar is subject to interference by chemicals present in oil or the presence of bacterial carbohydrates. Further studies are being conducted to establish standard protocols for the carbohydrate analysis in the context of measuring flowback and produced water quality monitoring.

Conflicts of interest

Declarations of interest: none.

Acknowledgements

This work was funded by the California Department of Conservation under Award Agreement 2015-022 and 2017-011 with Lawrence Berkeley National Laboratory. Emily Reader and

James Ackerman of the Division of Oil, Gas, and Geothermal Resources provided data and valuable guidance in completing this study. Preston Jordan and Jeremy Domen of Lawrence Berkeley National Laboratory provided valuable technical support. This study was supported in part by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH1123. This material includes work supported by the Department of Energy CERC-WET project under Award Number DE-IA0000018.

References

- 1 B. R. Scanlon, R. C. Reedy, F. Male and M. Walsh, Water issues related to transitioning from conventional to unconventional oil production in the Permian Basin, *Environ. Sci. Technol.*, 2017, **51**, 10903–10912.
- 2 B. R. Scanlon, R. C. Reedy and J. P. Nicot, Comparison of water use for hydraulic fracturing for unconventional oil and gas versus conventional oil, *Environ. Sci. Technol.*, 2014, **48**, 12386–12393.
- 3 W. T. Stringfellow, M. K. Camarillo, J. K. Domen, W. L. Sandelin, C. Varadharajan, P. D. Jordan, M. T. Reagan, H. Cooley, M. G. Heberger and J. T. Birkholzer, Identifying chemicals of concern in hydraulic fracturing fluids used for oil production, *Environ. Pollut.*, 2017, **220**, 413–420.
- 4 W. T. Stringfellow, M. K. Camarillo, J. K. Domen and S. B. C. Shonkoff, Comparison of chemical-use between hydraulic fracturing, acidizing, and routine oil and gas development, *PLoS One*, 2017, **12**, 1–19.
- 5 W. T. Stringfellow, J. K. Domen, M. K. Camarillo, W. L. Sandelin and S. Borglin, Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing, *J. Hazard. Mater.*, 2014, **275**, 37–54.
- 6 CCST, An Independent Scientific Assessment of Well Stimulation in California, Volume 1, Well Stimulation Technologies and their Past, Present, and Potential Future Use in California, retrieved from http://ccst.us/projects/hydraulic_fracturing_public/SB4.php, California Council on Science and Technology (CCST), Lawrence Berkeley National Laboratory, Pacific Institute, and Dr. Donald Gautier, LLC, Sacramento, CA, 2015.
- 7 CCST, An Independent Scientific Assessment of Well Stimulation in California, Volume 2, Generic and Potential Environmental Impacts of Well Stimulation Treatments, retrieved from http://ccst.us/projects/hydraulic_fracturing_public/SB4.php, California Council on Science and Technology (CCST), Lawrence Berkeley National Laboratory, Pacific Institute, and Dr. Donald Gautier, LLC, Sacramento, CA, 2015.
- 8 K. O. Maloney, S. Baruch-Mordo, L. A. Patterson, J. P. Nicot, S. A. Entekin, J. E. Fargione, J. M. Kiesecker, K. E. Konschnik, J. N. Ryan, A. M. Trainor, J. E. Saiers and H. J. Wiseman, Unconventional oil and gas spills: materials, volumes, and risks to surface waters in four states of the U.S., *Sci. Total Environ.*, 2017, **581–582**, 369–377.
- 9 M. C. McLaughlin, T. Borch and J. Blotvogel, Spills of hydraulic fracturing chemicals on agricultural topsoil: biodegradation, sorption, and co-contaminant interactions, *Environ. Sci. Technol.*, 2016, **50**, 6071–6078.
- 10 L. A. Patterson, K. E. Konschnik, H. Wiseman, J. Fargione, K. O. Maloney, J. Kiesecker, J. P. Nicot, S. Baruch-Mordo, S. Entekin, A. Trainor and J. E. Saiers, Unconventional oil and gas spills: risks, mitigation priorities, and state reporting requirements, *Environ. Sci. Technol.*, 2017, **51**, 2563–2573.
- 11 N. Shrestha, G. Chilkoor, J. Wilder, V. Gadhamshetty and J. J. Stone, Potential water resource impacts of hydraulic fracturing from unconventional oil production in the Bakken shale, *Water Res.*, 2017, **108**, 1–24.
- 12 J. S. Harkness, G. S. Dwyer, N. R. Warner, K. M. Parker, W. A. Mitch and A. Vengosh, Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: environmental implications, *Environ. Sci. Technol.*, 2015, **49**, 1955–1963.
- 13 N. Jabbari, F. Aminzadeh and F. P. J. de Barros, Hydraulic fracturing and the environment: risk assessment for groundwater contamination from well casing failure, *Stoch. Environ. Res. Risk Assess.*, 2017, **31**, 1527–1542.
- 14 E. Barbot, N. S. Vidic, K. B. Gregory and R. D. Vidic, Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing, *Environ. Sci. Technol.*, 2013, **47**, 2562–2569.
- 15 N. El Shaari, M. Kedzierski and T. L. Gorham, *Quantifying Guar Polymer Recovery Post Hydraulic Fracturing to Determine the Degree of Fracture Cleanup: A Field Study of the Point of Rocks Formation, California*, Paper SPE-93912-MS, Society of Petroleum Engineers (SPE), Western Regional Meeting, 30 March–1 April, Irvine, California, 2005.
- 16 L. O. Haluszczak, A. W. Rose and L. R. Kump, Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA, *Appl. Geochem.*, 2013, **28**, 55–61.
- 17 T. Hayes, *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition, 2009.
- 18 S. Y. Kim, P. Omur-Ozbek, A. Dhanasekar, A. Prior and K. Carlson, Temporal analysis of flowback and produced water composition from shale oil and gas operations: impact of frac fluid characteristics, *J. Pet. Sci. Eng.*, 2016, **147**, 202–210.
- 19 A. J. Kondash, E. Albright and A. Vengosh, Quantity of flowback and produced waters from unconventional oil and gas exploration, *Sci. Total Environ.*, 2017, **574**, 314–321.
- 20 M-I SWACO, *Fracturing Fluid Flowback Reuse Project: Decision Tree & Guidance Manual*, Petroleum Technology Alliance of Canada, Science and Community Environmental Knowledge, 2012.
- 21 J. Rosenblum, A. W. Nelson, B. Ruyle, M. K. Schultz, J. N. Ryan and K. G. Linden, Temporal characterization of flowback and produced water quality from a hydraulically

- fractured oil and gas well, *Sci. Total Environ.*, 2017, **596–597**, 369–377.
- 22 P. F. Ziemkiewicz and Y. T. He, Evolution of water chemistry during Marcellus Shale gas development: a case study in West Virginia, *Chemosphere*, 2015, **134**, 224–231.
 - 23 K. Abdullah, T. Malloy, M. K. Stenstrom and I. H. Suffet, Toxicity of acidization fluids used in California oil exploration, *Toxicol. Environ. Chem.*, 2017, **99**, 78–94.
 - 24 E. Sutra, M. Spada and P. Burgherr, Chemicals usage in stimulation processes for shale gas and deep geothermal systems: a comprehensive review and comparison, *Renewable Sustainable Energy Rev.*, 2017, **77**, 1–11.
 - 25 H. Chen and K. E. Carter, Characterization of the chemicals used in hydraulic fracturing fluids for wells located in the Marcellus Shale Play, *J. Environ. Manage.*, 2017, **200**, 312–324.
 - 26 E. G. Elliott, A. S. Ettinger, B. P. Leaderer, M. B. Bracken and N. C. Deziel, A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity, *J. Exposure Sci. Environ. Epidemiol.*, 2017, **27**, 90–99.
 - 27 U.S. EPA, *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0: Data Management and Quality Assessment Report. EPA/601/R-14/006*, U.S. Environmental Protection Agency, Washington, D.C., 2015.
 - 28 NRDC, *State Hydraulic Fracturing Disclosure Rules and Enforcement: A Comparison, IB:12-06-A*, National Resources Defense Council (NRDC), New York City, 2012.
 - 29 T. Kaplan, *Citing Health Risks, Cuomo Bans Fracking in New York State*, New York Times, 2014.
 - 30 K. Konschnik and A. Dayalu, Hydraulic fracturing chemicals reporting: analysis of available data and recommendations for policymakers, *Energy Policy*, 2016, **88**, 504–514.
 - 31 F. Pavley, *Senate Bill-4 Oil and Gas: Well Stimulation*, California Legislature, Sacramento, CA, 2013, ch. 313.
 - 32 DOGGR, SB 4 Well Stimulation Treatment Regulations, Final Text of Regulations, *Regulation, and Conservation of Oil and Gas Resources*, California Division of Oil, Gas, and Geothermal Resources (DOGGR), Sacramento, CA, December 30, 2014, 2014, ch. 4. development.
 - 33 W. T. Stringfellow, M. K. Camarillo and P. Jordan, *Status of Well Stimulation in California Since Implementation of SB-4 Regulations. Prepared for: California Division of Oil, Gas, and Geothermal Resources (DOGGR)*, Berkeley National Laboratory, Berkeley, CA, 2017.
 - 34 W. T. Stringfellow, H. Cooley, C. Varadharajan, M. Heberger, M. Reagan, J. K. Domen, W. Sandelin, M. K. Camarillo, P. Jordan, K. Donnelly, S. Nicklisch, A. Hamdoun and J. Houseworth, *Impacts of Well Stimulation on Water Resources*, California Council on Science and Technology, Sacramento, CA, 2015, ch. 2.
 - 35 J. R. Bowersox, in *Structure, Stratigraphy and Hydrocarbon Occurrences San Joaquin Basin*, AAPG, California, Pacific Section, 1990, pp. 215–223.
 - 36 T. W. Patzek, *Surveillance of South Belridge Diatomite, Paper SPE 24040, Society of Petroleum Engineers (SPE) Western Regional Meeting*, Bakersfield, California, 30 March-1 April, 1992.
 - 37 D. E. Schwartz, Characterizing the Lithology, Petrophysical Properties, and Depositional Setting of the Belridge Diatomite, South Belridge Field, Kern County, California, *Stud. Geol. San Joaquin Basin*, 1988, vol. 60, pp. 281–301.
 - 38 J. J. Stosur and A. David, Petrophysical evaluation of the diatomite formation of the Lost Hills Field, California, *J. Pet. Technol.*, 1976, **28**, 1138–1144.
 - 39 K. E. Peters, L. B. Magoon, Z. C. Valin and P. G. Lillis, *Source-Rock Geochemistry of the San Joaquin Basin Province*, U.S. Geological Survey, California, Professional Paper 1713, 2007.
 - 40 K. Bybee, Acid fracturing a carbonate reservoir, *J. Pet. Technol.*, 2004, **56**, 49–52.
 - 41 *Production Enhancement with Acid Stimulation*, ed. L. J. Kalfayan, PennWell Corporation, 2008.
 - 42 X. Liu, G. Zhao, L. Zhao and P. Liu, Acid fracturing technique for carbonate reservoirs using nitric acid powder, *J. Can. Pet. Technol.*, 2005, **44**, 46–52.
 - 43 M. K. Camarillo, J. K. Domen and W. T. Stringfellow, Physical-chemical evaluation of hydraulic fracturing chemicals in the context of produced water treatment, *J. Environ. Manage.*, 2016, **183**, 164–174.
 - 44 M. Elsner and K. Hoelzer, Quantitative survey and structural classification of hydraulic fracturing chemicals reported in unconventional gas production, *Environ. Sci. Technol.*, 2016, **50**, 3290–3314.
 - 45 U.S. EPA, *Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (Final Report). EPA-600-R-16-236*, U.S. Environmental Protection Agency, Washington, D.C., 2016.
 - 46 CA DWR, State Water Project, California Department of Water Resources (CA DWR), www.water.ca.gov/Programs/State-Water-Project, accessed May 17, 2018.
 - 47 C. A. Dieter, M. A. Maupin, R. R. Caldwell, M. A. Harris, T. I. Ivahnenko, J. K. Lovelace, N. L. Barber and K. S. Linsey, *Estimated use of water in the United States in 2015: U.S. Geological Survey Circular 1441*, U.S. Department of the Interior, U.S. Geological Survey, Washington, DC, 2018.
 - 48 R. B. Jackson, E. R. Lowry, A. Pickle, M. Kang, D. DiGiulio and K. G. Zhao, The depths of hydraulic fracturing and accompanying water use across the United States, *Environ. Sci. Technol.*, 2015, **49**, 8969–8976.
 - 49 K. Oetjen, K. E. Chan, K. Gulmark, J. H. Christensen, J. Blotevogel, T. Borch, J. R. Spear, T. Y. Cath and C. P. Higgins, Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse, *Sci. Total Environ.*, 2018, **619–620**, 654–664.
 - 50 F. Osselin, M. Nightingale, G. Hearn, W. Kloppmann, E. Gaucher, C. R. Clarkson and B. Mayer, Quantifying the extent of flowback of hydraulic fracturing fluids using chemical and isotopic tracer approaches, *Appl. Geochem.*, 2018, **93**, 20–29.
 - 51 A. J. Kondash, N. R. Warner, O. Lahav and A. Vengosh, Radium and barium removal through blending hydraulic fracturing fluids with acid mine drainage, *Environ. Sci. Technol.*, 2014, **48**, 1334–1342.
 - 52 A. Vengosh, R. B. Jackson, N. Warner, T. H. Darrah and A. Kondash, A critical review of the risks to water resources

- from unconventional shale gas development and hydraulic fracturing in the United States, *Environ. Sci. Technol.*, 2014, **48**, 8334–8348.
- 53 S. Hur, K. Nam, J. Kim and C. Kwak, Development of urban runoff model FFC-QUAL for first-flush water-quality analysis in urban drainage basins, *J. Environ. Manage.*, 2018, **205**, 73–84.
- 54 M. A. Cluff, A. Hartsock, J. D. MacRae, K. Carter and P. J. Mouser, Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus shale gas wells, *Environ. Sci. Technol.*, 2014, **48**, 6508–6517.
- 55 M. R. Rover, P. A. Johnston, B. P. Lamsal and R. C. Brown, Total water-soluble sugars quantification in bio-oil using the phenol-sulfuric acid assay, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 194–201.
- 56 Y. Lester, I. Ferrer, E. M. Thurman, K. A. Sitterley, J. A. Korak, G. Aiken and K. G. Linden, Characterization of hydraulic fracturing flowback water in Colorado: implications for water treatment, *Sci. Total Environ.*, 2015, **512**, 637–644.
- 57 J. L. Luek, M. Harir, P. Schmitt-Kopplin, P. J. Mouser and M. Gonsior, Temporal dynamics of halogenated organic compounds in Marcellus Shale flowback, *Water Res.*, 2018, **136**, 200–206.
- 58 S. J. Maguire-Boyle and A. R. Barron, Organic compounds in produced waters from shale gas wells, *Environ. Sci.: Processes Impacts*, 2014, **16**, 2237–2248.
- 59 A. J. Sumner and D. L. Plata, Halogenation chemistry of hydraulic fracturing additives under highly saline simulated subsurface conditions, *Environ. Sci. Technol.*, 2018, **52**, 9097–9107.

SUPPLEMENTARY MATERIALS

**Flowback versus First-Flush:
New Information on the Geochemistry of Produced Water from
Mandatory Reporting**

By

William T. Stringfellow^{a,b} and Mary Kay Camarillo^{a,b,*}

^aEcological Engineering Research Program, School of Engineering & Computer Science,
University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, USA.

^bEarth & Environmental Sciences Area, Lawrence Berkeley National Laboratory,
1 Cyclotron Road, Berkeley, CA 94720, USA.

*Corresponding author. Email: wstringfellow@lbl.gov Phone: +1-510-486-7903

Prepared for submission to:

Environmental Science: Processes & Impacts

October 2018

Table S-1. Chemical constituents used in well stimulations in California, May 5, 2015 – June 29, 2016, sorted by frequency of use in well stimulations. There were 618 stimulations conducted at 596 wells. The number of unique constituents is 178. TT= used as a tracer (chemical was used in a treatment where tracers were used), AF=used in acid fracturing, MA=used in matrix acidizing.

Chemical name	CASRN	Stimu- lations
Water	7732-18-5	618
Crystalline silica (quartz)	14808-60-7	617
Guar gum	9000-30-0	617
Ammonium persulfate	7727-54-0	577
2-Butoxypropan-1-ol	15821-83-7	522
1-Butoxy-2-propanol	5131-66-8	522
Prolonium chloride	55636-09-4	522 (AF)
Paraffinic petroleum distillate, hydrotreated light	64742-55-8	522
Isotridecanol, ethoxylated	9043-30-5	522
Magnesium nitrate	10377-60-3	521
Crystalline silica (cristobalite)	14464-46-1	521
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	521
2-Methyl-3(2H)-isothiazolone	2682-20-4	521
Hydrotreated light petroleum distillate	64742-47-8	521
Magnesium chloride	7786-30-3	521
Diatomaceous earth, calcined	91053-39-3	521
Sodium hydroxide	1310-73-2	519
Sodium tetraborate decahydrate	1303-96-4	493
Ethylene glycol	107-21-1	447
Phosphonic acid	13598-36-2	411
Nitrilotris (methylene phosphonic acid)	6419-19-8	410
Hemicellulase enzyme concentrate	9025-56-3	288
Glycerol	56-81-5	287
Sodium chloride	7647-14-5	276
Beta mannanases	37288-54-3	233
Methanol	67-56-1	84
Boric acid	10043-35-3	79
Methyl borate	121-43-7	79
Potassium bicarbonate	298-14-6	79
Potassium carbonate	584-08-7	79
Hemicellulase enzyme	9012-54-8	61
Non-crystalline silica (impurity)	7631-86-9	55
Isopropanol	67-63-0	53
Calcium magnesium sodium phosphate frit	65997-18-4	49
Choline chloride	67-48-1	49
Tetrakis hydroxymethyl phosphonium sulfate	55566-30-8	46
1,2-benzisothiazolin-3-one	2634-33-5	42

Chemical name	CASRN	Stimulations
Sodium polyacrylate	9003-04-7	41
Ammonium chloride	12125-02-9	40
Sodium sulfate	7757-82-6	40
Sodium persulfate	7775-27-1	40
Monoethanolamine borate	26038-87-9	39
Polydimethyl diallyl ammonium chloride	26062-79-3	39
Lactose	63-42-3	39
Sodium bisulfite	7631-90-5	39
Acetic acid	64-19-7	34
Triethanolamine	102-71-6	31
Zinc sulfate	7733-02-0	28
Xanthan gum	11138-66-2	22
Propylene glycol	57-55-6	22
Sodium citrate	68-04-2	22
Triethylene glycol	112-27-6	21 (AF)
Castor oil, ethoxylated	61791-12-6	21 (AF)
Alcohols, C12-15 ethoxylated	68131-39-5	21 (AF)
1,2-Ethanediamine, N1-(2-aminoethyl)-N2-(2-((2-aminoethyl)amino)ethyl)-, polymer with 2-methyloxirane and oxirane	68815-65-6	21 (AF)
Poly(oxy-1,2-ethanediyl), .alpha.-2,4,6-tris(1-phenylethyl)phenyl-.omega.-hydroxy-	70559-25-0	21 (AF)
Sorbitan stearate	1338-41-6	20
2-Propenoic acid, 2-ethylhexyl ester, polymer with 2-hydroxyethyl 2-propenoate	36089-45-9	20
Tetrahydro-3,5-dimethyl-1,3,5-thiadiazine-2-thione	533-74-4	20
Dimethyl siloxanes and silicones	63148-62-9	20
Siloxanes and silicones, dimethyl, reaction products with silica	67762-90-7	20
Fatty acids, C18-unsatd., dimers, ethoxylated propoxylated	68308-89-4	20
Siloxanes and Silicones, di-Me, 3-hydroxypropyl Me, ethoxylated propoxylated	68937-55-3	20
Sodium nitrite	7632-00-0	20
Sodium carboxymethylcellulose	9004-32-4	20
Sorbitan monooleate, ethoxylated	9005-65-6	20
Citrus terpenes	94266-47-4	19
Potassium chloride	7447-40-7	15
Polypropylene glycol	25322-69-4	9
Citric acid	77-92-9	9
Glutaraldehyde	111-30-8	8
MBNPA (2-bromo-3-nitrilopropionamide)	1113-55-9	8
D-limonene	5989-27-5	8
2,2 Dibromo-3-nitrilopropionamide	10222-01-2	7
Lauryl hydroxysultaine	13197-76-7	7

Chemical name	CASRN	Stimu- lations
Acetic acid ethenyl ester, polymer with ethene	24937-78-8	5
Diatomaceous earth, natural (kieselguhr)	61790-53-2	5
Heavy aromatic naphtha	64742-94-5	5
Olefin/maleic ester	68188-50-1	5
Mineral oil	8042-47-5	5
Naphthalene	91-20-3	5
1,2,4-Trimethylbenzene	95-63-6	5
Acrylonitrile	107-13-1	4
Potassium acetate	127-08-2	4
Potassium hydroxide	1310-58-3	4
Potassium borate	1332-77-0	4
4-Chlorobenzophenone	134-85-0	4 (TT)
Magnesium silicate hydrate (talc)	14807-96-6	4
Vinylidene chloride/methylacrylate copolymer	25038-72-6	4
Polyethylene glycol monohexyl ether	31726-34-8	4
Polytetrafluoroethylene	9002-84-0	4
2-propenoic acid, polymer with 2-propenamide	9003-06-9	4
1,4-Dibromobenzene	106-37-6	3 (TT)
1-bromo-3,5-dichlorobenzene	19752-55-7	3 (TT)
Poly(dimethylaminoethylmethylacrylate) dimethyl sulphate quat.	27103-90-8	3
2,5-Dibromothiophene	3141-27-3	3 (TT)
1-Bromo-4-iodobenzene	589-87-7	3 (TT)
Dicoco dimethyl quaternary ammonium chloride	61789-77-3	3
4-Iodotoluene	624-31-7	3 (TT)
1,3,5-Tribromobenzene	626-39-1	3 (TT)
2,4,6-Tribromotoluene	6320-40-7	3 (TT)
1,2,4,5-Tetrabromobenzene	636-28-2	3 (TT)
1-Chloro-4-iodobenzene	637-87-6	3 (TT)
Orange terpenes	68647-72-3	3 (AF)
Ethoxylated alcohol C11-14	78330-21-9	3
Phenolic resin	9003-35-4	3
1-Iodonaphthalene	90-14-2	3 (TT)
2-Ethylhexan-1-ol	104-76-7	2
Ethoxylated alcohol C6	104780-82-7	2
2-Butoxyethanol	111-76-2	2
Disodium octaborate tetrahydrate	12008-41-2	2
Corundum	1302-74-5	2
Ulexite	1319-33-1	2
Mullite	1327-36-2	2
3,5-Dibromotoluene	1611-92-3	2 (TT)
2,4,5-Tribromotoluene	3278-88-4	2 (TT)
1,2-Diiodobenzene	615-42-9	2 (TT)

Chemical name	CASRN	Stimulations
Hydrochloric acid	7647-01-0	2
Hydrofluoric acid	7664-39-3	2
Zirconium dichloride oxide	7699-43-6	2
Ethoxylated alcohol C7-9-iso, C8	78330-19-5	2
Polyethylene, polypropylene ether glycol copolymer	9003-11-6	2
Calcium chloride	10043-52-4	1
Quaternary ammonium compound	100765-57-9	1 (AF)
Cinnamaldehyde	104-55-2	1 (AF)
Propargyl alcohol	107-19-7	1
1-Methoxy-2-propanol	107-98-2	1
Methyl isobutyl ketone	108-10-1	1 (AF)
Diethanolamine	111-42-2	1
2,2"-oxydiethanol (impurity)	111-46-6	1
1-Tetradecene	1120-36-1	1
Oleic acid	112-80-1	1
1-Octadecene	112-88-9	1
Ammonium fluoride	12125-01-8	1
2-Propenoic acid, polymer with sodium phosphinate	129898-01-7	1
Ammonium bifluoride	1341-49-7	1
Potassium oleate	143-18-0	1
2-Iodobiphenyl	2113-51-1	1 (TT)
5-Iodo-m-xylene	22445-41-6	1 (TT)
Polyethylene oxide	25322-68-3	1
Dodecylbenzene sulfonic acid	27176-87-0	1
Etidronic acid	2809-21-4	1
4-Iodo-o-xylene	31599-61-8	1 (TT)
1-Eicosene	3452-07-1	1
Aziridine, polymer with methyloxirane and oxirane	52501-07-2	1 (AF)
Hydroxylamine hydrochloride	5470-11-1	1 (MA)
Polyurethane resin	57029-46-6	1
9-Bromophenanthrene	573-17-1	1 (TT)
Diethyl sulfosuccinate sodium salt	577-11-7	1
2-Bromonaphthalene	580-13-2	1 (TT)
3-aminopropyl (sileanetriol)	58160-99-9	1
Fatty acids, tall-oil	61790-12-3	1
Amines, hydrogenated tallow alkyl, acetates	61790-59-8	1
Fatty acids, tall-oil, ethoxylated	61791-00-2	1 (AF)
1-Hexadecene	629-73-2	1
Ethanol	64-17-5	1
Formic acid	64-18-6	1
Benzoic acid	65-85-0	1 (AF)
Alcohols, C10-14, ethoxylated	66455-15-0	1
Sulferized polyolefin	68037-13-8	1 (AF)

Chemical name	CASRN	Stimulations
Phenol, 4,4'-(1-methylethylidene) bis-, polymer with 2-(chloromethyl)oxirane, 2-methyloxirane and oxirane	68123-18-2	1
Silanetrio; (3-aminopropyl, homopolymer	68400-07-7	1
Ethoxylated alcohol C6-12	68439-45-2	1
Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	1
Alcohols, C12-16, ethoxylated	68551-12-2	1
Ethoxylated alcohol C8-10	68603-25-8	1 (AF)
Alcohols, C14-C15, ethoxylated	68951-67-7	1
2,4-Dibromomesitylene	6942-99-0	1 (TT)
Tar bases, quinoline derivs., benzyl chloride quaternized	72480-70-7	1 (AF)
Copper dichloride	7447-39-4	1 (MA)
Ethylene oxide	75-21-8	1
Sulfuric acid	7664-93-9	1
Potassium iodide	7681-11-0	1
Triisobutylene (mixed isomers)	7756-94-7	1 (AF)
Tricalcium phosphate	7758-87-4	1
Polyethylene glycol trimethyl nonyl ether	84133-50-6	1
Erythorbic acid	89-65-6	1