

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

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3 Environmental Significance Statement
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5 William T. Stringfellow and Mary Kay Camarillo
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8 Mandatory Reporting
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12 Mandatory reporting by industry allowed detailed analysis of hydraulic fracturing practices,
13 including comparison of chemical use and produced water quality by geological formation. The
14 pseudo-plug-flow conceptual model of flowback developed in shale formations, where salinity
15 increases over time as produced water is extracted, was not applicable to unconventional wells in
16 these oil reservoirs, which are predominately diatomite and sandstones. In these formations
17 stimulation caused a “first-flush” phenomena, where salts and metals were initially high and then
18 decreased in concentration over time, as more produced water was extracted. New information
19 on acid treatments and the use of chemical indicators of flowback indicate that acid fracturing
20 treatments are infrequently applied and the use of chemical indicators needs to be further
21 validated.
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FULL LENGTH ARTICLE

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

by

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Abstract

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.

Key Words

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3 Oil and gas production; Produced water; Flowback; Matrix acidizing; Acid fracturing; Hydraulic
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5 fracturing;
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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 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

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3 shales or tight-rock, except one that was conducted in a sandstone.¹⁵ In this paper, we examined
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5 flowback and produced water from diatomite and sandstone formations. Pseudo-plug-flow has
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7 become a common conceptual model of how flowback will behave, but how and when well
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9 stimulation chemicals and their degradation products “return” from the well with the produced
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11 water is an active area of research.
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15 Several studies have taken a fundamental approach to characterizing the hazards and risks
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17 associated with well stimulation fluids by examining the chemical composition of the stimulation
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19 fluids injected into oil and gas wells. Most hazard analyses have focused on hydraulic fracturing,
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21 but some studies have also characterized chemical hazards associated with acid stimulation
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23 formulations.^{4, 23, 24} These studies identified persistent data gaps concerning which chemicals are
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25 used in well stimulation and their corresponding frequency of use, masses applied, and missing
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27 physical-chemical and toxicological information.^{3, 25-27} Most of these studies have been limited
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29 by their dependence on information voluntarily disclosed by the oil and gas industry which
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31 prevents a definitive conclusion concerning well stimulation practices, since the completeness of
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33 the information is unknown.⁴ The reliance on voluntary disclosures has undermined public
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35 confidence in the safety of well stimulation, and stakeholders—the public, environmental groups,
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37 consumer advocates, scientists, and regulators—have sought more information and greater
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39 transparency concerning well stimulation practices.²⁸ This persistent lack of information has led
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41 some states and localities to limit or even ban hydraulic fracturing.²⁹
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47 Oil and gas production is typically regulated on a state-by-state basis. In order to close
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49 data gaps, improve oversight, and respond to public concerns about the safety of hydraulic
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51 fracturing and other well stimulation activities, states are instituting new laws and regulations
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53 requiring mandatory reporting of a variety of information on well stimulation activities, most
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3 typically the location of stimulation treatments and chemical formulation of well stimulation
4 fluids.^{30,31} In California, *Senate Bill No. 4 – Well Stimulation: Oil and Gas* (SB-4), which went
5 into effect in January 2014, was promulgated with the goal of providing greater transparency
6 concerning well stimulation practices.³¹ In addition to mandating disclosure of well stimulation
7 locations and formulations, SB-4 regulations also require water quality analysis of the water used
8 for stimulation fluids (base-fluid), water quality analysis of produced water during the first three
9 well-volumes of flow, and water quality analysis after 30 days of production.³² The timing of the
10 sampling for water quality analysis was based on the plug-flow conceptual model, where the first
11 sampling (within three well volumes) would characterize the injectate flowback and the second
12 sampling (on or about 30 days after production) would represent the quality of the connate water
13 that would be produced with oil over the life of the well. The SB-4 regulations include the
14 requirement that the producer measure a chemical characteristic of the well stimulation fluid
15 (indicator chemical) as part of the water quality characterization of the produced water.^{31,32} In all
16 but one hydraulic fracture included in this study applied guar gum as a gelling agent and used the
17 measurement of total carbohydrates as a chemical indicator. Guar gum is used extensively as a
18 gelling agent in hydraulic fracturing fluids both in California and nationally.^{4,5}

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

23 **2.1. Data sources**

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26 Well stimulation disclosure data, collected per SB-4 requirements,³² were obtained from
27 the Division of Oil, Gas, and Geothermal Resources (DOGGR).³³ The disclosure data includes
28 the dates of well stimulation, locations, chemicals used and masses, water volumes, base-fluid
29 water quality, produced water quality, the production company producing the oil and gas
30 (producer), and the supplier of stimulation chemicals and formulations (service company). The
31 data set included water quality results from two samples from each well. The first sample was
32 collected within the first three wellbore volumes of flow, and the second sample was collected
33 approximately 30 days after the start of production and the collection of the first sample.³² The
34 disclosure data evaluated represents 618 well stimulations occurring at 596 wells between May
35 2015 and June 2016. There were 616 hydraulic fracturing treatments, one matrix acidizing
36 treatment, and one acid fracturing treatment. The majority of wells (575) had only one
37 stimulation treatment, although two or three stimulations were completed at other wells. All well
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3 stimulations took place in Kern County with the exception of one hydraulic fracturing treatment
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5 in Orange County.
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8 Other sources of data included the state's oil and gas production database, which includes
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10 produced water volumes that were downloaded from the DOGGR website on February 6, 2017.
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12 Produced water volumes were used to estimate the volume of fluid recovered from wells at the
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14 time of the second sample. Volumes of fluid recovered at the time of the first sample were
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16 reported with the disclosure data. Other data used included well production start dates that were
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18 provided directly by the DOGGR on January 27, 2017. Where sample collection occurred prior
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20 to well production, a value of "0" was assigned to the days between the start of production and
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22 sample collection (for plotting). Rig release dates were provided by the DOGGR on February 17,
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24 2017. Rig release is indicative of well age, as it occurs when oil and gas drilling and completion
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26 equipment and associated structures were last used at a well site.
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31 Mandatory disclosure data were compared with voluntary disclosure data for chemicals
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33 used in hydraulic fracturing in California, as reported to the FracFocus registry, versions 1 and 2
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35 (FF12), as summarized by Stringfellow et al.^{3,34} Mandatory data were also compared with data
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37 collected for chemical use in routine oil and gas production (well drilling, completion, and
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39 rework activities) in Southern California (Orange County and parts of Los Angeles, San
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41 Bernardino, and Riverside counties), as reported to the South Coast Air Quality Management
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43 District (SCAQMD) and summarized by Stringfellow et al.⁴
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47 **2.2. Geology**

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49 The majority of well stimulations occurred in the South Belridge oilfield (536
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51 treatments), with additional stimulations being completed in Lost Hills (58 treatments), North
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53 Belridge (12), Elk Hills (5), McKittrick (4), North Coles Levee (2), and Brea-Olinda (1) oilfields
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(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). Chemicals 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.

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

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) plus the TDS of water used to formulate stimulation fluids.

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3 In calculating the number of unique constituents per stimulation, multiple entries for a
4 single constituent were pooled to avoid double-counting. Proppants were separated from carriers,
5 assuming that proppants consisted of mineral solids (e.g. crystalline quartz) with mass
6 concentrations greater than one percent.
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11 **2.4. Analysis software and methods**

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

32 **3.1. Well stimulation treatments**

33 All well stimulation treatments were hydraulic fracturing operations conducted using
34 formulations containing guar gum (gel treatments), with the exception of one matrix acidizing
35 treatment and one acid fracturing treatment (Table 1). The chemicals used for acid fracturing and
36 matrix acidizing are identified in Table S-1. Of the chemicals reported as used in matrix
37 acidizing and acid fracturing, seventeen chemicals had not been reported previously under
38 voluntary reporting requirements.^{3, 4, 34} There is limited published information on acid treatments,
39 including matrix acidizing and acid fracturing,^{4, 23, 40-42} and the SB-4 regulations are helping
40 close the data gap concerning acid treatments identified in previous studies concerning chemical
41 use and frequency of application in California.^{6, 7}
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3 A complete list of the chemicals used for well stimulation on California between May
4 2015 and June 2016 is given in Table S-1. There were 54 stimulation chemicals identified via
5 mandatory reporting under SB-4 that had not been identified in previous studies.^{3, 4, 34} The newly
6 identified chemicals were used infrequently (in less than 10% of well stimulations), except the
7 clay control agent hydroxytrimethylene bis(trimethylammonium) dichloride (55636-09-4), which
8 was used in 84% of treatments (522 treatments). Previously in California, as revealed by
9 voluntary reporting, a different clay control agent, 1,2-ethanediaminium, N1,N2-bis[2-[bis(2-
10 hydroxyethyl)methylammonio]ethyl]-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-, chloride
11 (1:4) (138879-94-4), was used in most frequently (66% of all treatments).^{3, 34} The reason for this
12 change in clay-control strategy is not known and may be inconsequential from a risk
13 management perspective, but in the absence of publicly available information on the toxicity,
14 biodegradability, or other environmentally critical properties of clay control agents it may be
15 premature to dismiss risk from these materials altogether.^{3-5, 43}

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33 Twenty of the newly identified chemicals were chlorinated, brominated, or iodated
34 aromatic hydrocarbons (Table S-1). Halogenated aromatic compounds can be environmentally
35 persistent and toxic, so there is specific interest in the use of these types of compounds in the
36 context of produced water reuse and risk assessment.³ While environmentally persistent, these
37 compounds appear to have been used as tracers and tracer-tests were only conducted in eight
38 well stimulations, suggesting use of these chemicals is not routine. The halogenated
39 hydrocarbons were used in approximately 1% of all treatments and at doses of < 1 kg per
40 treatment. To our knowledge, this is the first time the use of these chemicals has been
41 acknowledged in California, illustrating the value of mandatory reporting for evaluating the
42 hazards and risks associated with well stimulation and other oil-field practices.

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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 Figure 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 35% (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 TDS was 58% (9,000 mean \pm 5,300 standard deviation); guar gum was 24% (2,500 \pm 600 mg/L); and boron CV was 36% (50 \pm 18 mg/L).

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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(2H)-isothiazolone (26172-55-4) and 2-methyl-3(2H)-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

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

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3 should be welcome news for regulators. There may be many different reasons for treatments to
4 differ widely, even within the same geological zone, including geological heterogeneity, well
5 depth, economic decisions, intellectual property, and operational preferences, but these results
6 suggest that there is a consistence to on-field practices that serves to increases the predictability
7 or reliability of risk assessment efforts.
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14 **3.2. Water use for well stimulation**

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17 As the result of new reporting requirements under SB-4 regulation, information is now
18 available on the quality of waters used as base-fluid for well stimulation formulations (Table 3).
19 The predominated source of water for fluid formulation is surface water from the California
20 Aqueduct, which is appropriate for other beneficial uses, as indicated by salinity between 150 –
21 540 mg/L TDS (Table 3). In addition to fresh surface water, there was some use of brackish
22 groundwater (4,400 – 6,400 mg/L TDS) and recycled produced water (10,000 – 38,000 mg/L
23 TDS) for fluid formulation, although use of alternative water supplies was not common. The
24 California Aqueduct is a major source of fresh water for California, which puts water use for
25 well stimulation in direct competition with demand by urban and agricultural uses, however, the
26 total quantity of water used in all well stimulations during the studied period was approximately
27 230,000 m³, which is a small fraction of the aqueduct capacity and the estimated 13 trillion m³
28 annual surface water use in California.^{46, 47} Requiring characterization of the water quality of the
29 water used as a bulk-fluid for formulation closes an important data gap identified in previous
30 studies⁶ and is useful for understanding the phenomena of flowback in the context of produced
31 water.
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51 The volume of water used was a function of stimulation zone length, but also varied by
52 the reservoir geological properties as indicated by FAP code (Figure 2). Overall, the mean (\pm
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3 standard deviation) and median volume of water used was 421 +/- 334 m³ and 381 m³ per
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5 stimulation, respectively, which is consistent with estimates made in previous studies concerning
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7 California oil fields and less than the average water use of 9,200 m³ per treatment in the U.S.
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9 overall.^{34, 48} The intensity of water use (volume of water per length of stimulation zone) was
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11 largely consistent within oil fields independent of operator or service company (Table 1), with
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13 water intensity being higher in the Lost Hills field (3.8 ± 1.38 m³/m) than North Belridge ($1.68 \pm$
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15 0.10 m³/m) or South Belridge (1.59 ± 0.87 m³/m).
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20 Mandatory reporting offered a unique opportunity to compare water use intensity
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22 between companies operating in the same FAP (Table 1). In the same FAP (4320027), one
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24 company had a water use intensity more than twice that of another company (Table 1, 2.0 ± 0.14
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26 m³/m versus 4.6 ± 0.82 m³/m). The two service companies also used different chemical
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28 formulations (Figure 1, Table 2), with the treatments with greater water intensity using less
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30 chemicals in this case. Comparison of different practices within the same FAP (Figure 1)
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32 suggests that there are opportunities for companies to modify hydraulic fracturing practices to
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34 improve water conservation and, perhaps, utilize green-chemistry alternatives.
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38 **3.3. Temporal characterization of produced water chemistry in context of a plug –flow** 39 40 **model**

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42 The most common conceptual model for produced water extracted from hydraulically
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44 fractured wells is the pseudo-plug-flow model, where the initial flush of water from the well will
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46 be a flowback of injected fluid followed by a transition to connate water from the formation. A
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48 characteristic of this model is that samples collected at early time points are expected to be at
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50 lower concentration than samples collected at later time points, until a maximum concentration is
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52 reached (e.g. ^{49, 50}). The SB-4 requirement for sampling at the initial flow from the well and then
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3 again after the well has been produced for a month is based on this model.^{7, 32} We compared the
4 water quality of the initial sampling and the final sampling taken from the same well to test the
5 hypothesis that the initial flow will consist of well stimulation fluid flowback. This analysis was
6 conducted for the three oil fields (South Belridge, North Belridge, and Lost Hills) which
7 sufficient replicate data was available (Table 1).
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11 Table 4 compares initial and final water quality for samples taken at approximately three
12 well volumes and after thirty days as required by SB-4 well stimulation regulations.³² In contrast
13 to what would be expected from the pseudo-plug-flow flowback model, for most constituents the
14 concentration measured in the initial sample was higher than the final concentration (Table 4).
15 For example, the mean TDS was over 66,000 mg/L for the initial samples and declined to less
16 than 27,000 mg/L in later samples (Table 4 and Figure 3). In comparison, the salinity of the
17 injected fluid is approximately 9,000 mg/L TDS, suggesting the injectate flowback has little
18 direct influence on the initial produced water quality. The mean recovered flow at the initial
19 sampling was $54 \pm 157 \text{ m}^3$, which represents 16% of the injected fluid volume, and the final
20 sample was taken at $815 \pm 521 \text{ m}^3$, which is equivalent to 228% of the injected volume.
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38 Many constituents were significantly higher in the first sample than the second, as
39 determined by paired t-test of initial and final samples from the same well (Table 4). Ions, such
40 as chloride, calcium, potassium, magnesium, and sodium, and metals, including copper, iron, and
41 zinc, were higher in the initial sample than the final sample. Radioactive materials, including
42 radium (Ra-226 and Ra-222), beta-counts, and alpha-counts, were also higher in the initial
43 samples than the final samples (Table 4). This result is notable because the radioactivity of
44 surface waters used in most fluid formulations was low (Table 4), which clearly demonstrates
45 that radioactive materials found in higher concentrations in the initial sample are derived from
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3 material extracted from the reservoir geology, rather than representing a signal of flowback of
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5 the injected fluid.
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8 The stimulation fluids are likely mobilizing sorbed inorganic chemicals, including
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10 radioactive materials, from within the formation,^{51, 52} however, it should be noted that the highest
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12 Ra-226 value observed in this produced water, 917 pCi/L, was an order of magnitude lower than
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14 that observed in gas wells.^{14, 16, 21, 22} As an example, Barbot et al.¹⁴ measured Ra-226 as high as
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16 9,280 pCi/L in northeastern Pennsylvania.
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19 From this analysis we propose a “first-flush” model, where hydraulic fracturing disturbs the
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21 formation and extracts minerals from reservoir rocks, which are then brought to the surface with
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23 produced water. First flush phenomena are common in other environmental process, including
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25 storm-water drainage, where sudden inputs of fluid and energy disrupt system equilibrium (e.g.
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27 ⁵³). A characteristic of this model is that earlier samples may be of higher concentration than
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29 later samples. The model of flowback returning as a pseudo-plug-flow is not applicable to these
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31 oil reservoirs (Table 1) and perhaps not to reservoirs of migrated oil in general, which tend to
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33 contain more water than source-rock. Prior studies that observed pseudo-plug-flow flowback
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35 were conducted in shale and “tight-rock” formations and examined gas or shale-oil production
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37 from source-rock,^{14, 16-22} whereas this study examined production of migrated oil from diatomite
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39 and sandstone (Table 1). There is some evidence that a first-flush phenomena can occur in
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41 shales, indicated by higher initial concentrations of various constituents or and increase to a peak
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43 concentration followed by a decline to a steady concentration, presumably representative of the
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45 connate water.^{17, 20, 54}
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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 used to further investigate the changes in water quality over time. Data were analyzed by geological formation (FAP) and changes in water quality was evaluated as a function of time from when the well was put into production (Figure 3). The majority of hydraulic fracturing stimulations occurred in the South Belridge oilfield FAP 0520020 and these data are presented in Figure 3.

In Figure 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 and then declined over time, trending toward an equilibrium concentration of about 10,000 to 40,000 mg/L. 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

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3 increases can also be more gradual, occurring over more than one year following the start of
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5 production.²¹ However, it has been observed that in some cases the TDS can peak and then start
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7 to decline.^{17, 20, 54}
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10 In this study, the trend is for the initial flow to be higher in salinity followed by a
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12 transition over a period of days toward less variation and a lower salinity, presumably more
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14 representative of the formation fluid. Both paired and grouped t-tests ($\alpha = 0.05$) show that
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16 injected fluids are significantly less concentrated in salts and boron than either the first sample or
17
18 the final sample. Figure 4 shows a comparison of the injectate fluid salinity to the salinity of the
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20 first and final samples for FAP 0520020, where the most samples were collected. The statistical
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22 analysis supports the temporal analysis by field (Figure 3) and is consistent with the results of
23
24 paired analysis for these stimulated wells (Table 4). The collection of only two samples per well
25
26 does not allow modeling of individual wells, but all of the statistical and graphic analysis
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28 supports the conclusion that flowback and pseudo-first order flows are not being observed in
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30 these formations, and that a first-flush conceptual model is more appropriate in the context of
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32 produced water management from these wells.
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38 **3.5. Indicators of stimulation fluids in produced water**

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40 Regulations governing well stimulation in California require that, as part of their water
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42 quality monitoring program, producers select and measure a chemical component characteristic
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44 of their well stimulation fluid in produced water from stimulated wells.³² The purpose of this
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46 measurement is to help characterize flowback and identify well stimulation chemicals in
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48 produced water over time. In most cases, operators measured total carbohydrates as an indicator
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50 of hydraulic fracturing fluid in produced water. Total carbohydrates was intended to measure
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52 residual gelling agents originating from stimulation fluids since guar gum is used extensively in
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3 hydraulic fracturing.^{5, 15} Guar gum was used in 617 of the 618 well stimulation treatments (Table
4 S-1), with a mean concentration of $2,500 \pm 600$ mg/L in the stimulation fluid. However, the use
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6 of the total carbohydrate as an indicator has not been validated and there is not a standard or
7
8 approved method for carbohydrate measurement in produced water.
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12 In order to investigate the utility of measuring carbohydrate as an indicator chemical, a
13 paired t-test was performed between initial and final water quality results for individual wells.
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15 This analysis indicated that measurement for total carbohydrate concentration did not change
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17 over time. The mean total carbohydrate concentration was 187 ± 156 mg/L in the initial sample
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19 versus $188 \text{ mg/L} \pm 173 \text{ mg/l}$ for the last sample from the same well. A temporal analysis of
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21 carbohydrate concentration over time was conducted and this analysis also indicated total
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23 carbohydrate did not change over time (Figure 3). This result is unexpected. After stimulation,
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25 guar gum is dissolved with breaker chemicals (typically enzymes) for the expressed purpose of
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27 releasing the guar from the formation, so it was expected that initial guar concentrations would
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29 be high and decline over time. Additionally, most other constituents did not show a steady or
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31 constant concentration between first and second samples or over time (Table 4, Figure 3).
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38 The results of this analysis indicate that either a) guar is returning at a consistent rate of
39 approximately 180 mg/L for the duration of the sampling period; or b) the carbohydrate method
40 is subject to interference and is giving a false positive measurement for carbohydrate; or c) that
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42 there is another sources of carbohydrate than guar gum in oil reservoirs. It seems unlikely to the
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44 authors, given the biodegradability of guar gum and the variability of the other water quality
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46 parameters, that there is a consistent flow of 180 mg/L guar from the well over time. The more
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48 likely interpretation of the result is that there is an interference that gives a false positive result
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50 for carbohydrates or that there is another source of carbohydrates in produced water.
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3 Recent studies in our laboratory have shown that produced water from wells that were not
4 hydraulically fractured can also be positive for carbohydrate by the anthrone and phenol methods
5 (data not shown). Previous studies have shown that aldehydes and other chemicals can interfere
6 with the carbohydrate test (e.g. ⁵⁵). Studies are on-going to determine if there is a chemical
7 interference or if there may be another source of carbohydrates in produced water. One
8 hypothesis being investigated is that bacteria may be a source of carbohydrates in produced
9 water.
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19 Total carbohydrate analysis is not yet a State certified or Standard Method and current
20 analysis may have insufficient quality control. Further studies are being conducted to establish
21 standard protocols for the carbohydrate analysis in the context of water quality monitoring, to
22 determine the applicability of the analysis to produced waters, and to develop methods for the
23 measurement of alternative and perhaps more appropriate indicator compounds in produced
24 water.
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33 **3.6. Other water quality parameters as indicators of injected fluid flowback**

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35 We investigated if other measurements indicated that injected fluids were flowing back
36 with produced water. Of all the parameters measured only five other constituents or parameters
37 (alkalinity, boron, bromium, hydrogen sulfide, and pH) showed a significant increase between
38 first and last sample events (Table 4). Of these parameters, alkalinity and boron were considered
39 further as indicators of hydraulic fracturing fluid flowback.
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47 Although alkalinity is not a specific parameter for well stimulation fluid, alkalinity gave
48 the strongest signal indicative of a flowback type phenomena of all the water quality parameters
49 measured, in that the alkalinity in produced water tended to increase over time (Figure 3). In the
50 initial samples in South Belridge FAP 0520020, the alkalinity was variable and frequently low,
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3 even less than 100 mg/L as CaCO₃ and within two days after the start of production, the
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5 alkalinity was higher, typically 1,000 – 5,000 mg/L as CaCO₃ (Figure 3). By the 30 day period
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7 the produced water shows a stable alkalinity of 1,000 to 5,000 mg/L as CaCO₃ and appears to be
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9 representative of formation fluids.
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12 The alkalinity of the stimulation fluids were not reported, but some information about
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14 injectate alkalinity is known. Water sources used in formulating stimulation fluids had moderate
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16 to low alkalinities alkalinity values (< 1,000 mg/L as CaCO₃). The most frequently used base
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18 fluid was surface water which had an alkalinity of 44 – 91 mg/L as CaCO₃ (Table 3). Although
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20 the hydraulic fracturing fluids can contain a variety of acids, including oleic acid, boric acid,
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22 phosphonic acid, acetic acid, and citric acid, acids were only added in 20% of the applications,
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24 with the exception of phosphonic acid which was added to 67% of the treatments. Phosphonic
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26 acid is a corrosion and scale inhibitor and carboxylic acids are frequently added to hydraulic
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28 fracturing fluids as chelating agents for scale and iron control rather than pH adjustment.³ In fact,
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30 bases were used more frequently in stimulation fluids than acids, with sodium hydroxide (1310-
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32 73-2) being used in 519 out of 616 hydraulic fracturing treatments (84%). Given the infrequent
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34 use of acids and the frequent use of bases, it seems unlikely that the initial low in alkalinity is the
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36 result of the stimulation fluids and is more likely a signal from acidic well-cleaning solutions.
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38 Since acids and potentially other cleaning solutions are used on both stimulated (unconventional)
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40 and conventional wells,⁴ future studies should consider comparing water quality between
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42 conventional and unconventional sources of produced water.
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49 Alkalinity is a poor indicator in the context of indicating injected fluid return-flow
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51 because of the lack of specificity of the measurement, but changes in alkalinity have been used to
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53 indicate flowback in previous studies. In studies of unconventional gas wells, alkalinity has been
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3 shown to decrease over time,^{14, 21} or to first increase to a peak and decrease,⁴⁹ but changes in
4 alkalinity can result from biological or chemical transformations, including mineral dissolution
5 or precipitation within the formation.^{14, 54} The alkalinity measurements in produced water also
6 need to be interpreted with caution because produced waters can contain high concentrations of
7 acetic acid or other similar carboxylic acids, that have pKa values near the total alkalinity end
8 point (~4.5) and can interfere with measurements of alkalinity.⁵⁶
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17 **3.7. Boron as an indicator of injected fluid flowback**

19 Boron is a common ingredient in gel treatment formulations, so the use of boron as an
20 indicator compound of stimulation fluid flowback deserves some consideration. All of the
21 hydraulic fracturing treatments contained boron, with an average concentration of 50 ± 18 mg/L.
22 Boron was added to hydraulic fracturing fluids in a number of forms, including boric acid
23 (10043-35-3), methyl borate (121-43-7), sodium tetraborate decahydrate (1303-96-4), and
24 monoethanolamine borate (26038-87-9) (Table S-1). Additionally, in a few cases, the bulk-fluid
25 also contained significant concentrations of boron (Table 3).
26

27 Boron concentration increased from an initial concentration of ~ 90 mg/L at 3 well
28 volumes to ~100 mg/L after a month of well production (Table 4). Paired t-test analysis of first
29 and last samples from individual wells indicate that this difference is significant (Table 4).
30 Although it is possible that boron concentration was lower in initial produced water samples due
31 to dilution of connate water with flowback, the results are far from conclusive. Diluent effects
32 could also occur from the use of well clean-out solutions. The sampling results do show that
33 produced waters contain significant concentrations of boron, which could impact their value for
34 reuse, either on-field or for agriculture.
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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

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3 radium, beta-counts, and alpha-counts, were also higher in produced water initially and declined
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5 over time. This result is in contrast to previous studies that found the salinity of the produced
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7 water from stimulated wells typically increased over time, fitting a conceptual model for pseudo-
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9 plug-flow, where the injected fluid returns before significant connate water is produced.¹⁴⁻²²

12 The difference in the observation of first-flush versus pseudo-plug-flow can be explained
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14 at least in part by differences in geology. Previous studies have mostly characterized produced
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16 water and flowback phenomena in hydraulically fractured source-rock: shales or tight-rock.<sup>14, 16-
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18 22</sup> Many of these studies occurred in gas fields, which typically produce less connate water than
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20 oil fields. In contrast, this study investigated produced water and flowback phenomena in
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22 migrated oil reservoirs (not source-rock) located in diatomite, sandstone, and carbonate
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24 formations (Table 1). The model of flowback returning as a pseudo-plug-flow is not applicable
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26 to these oil reservoirs and perhaps not to reservoirs of migrated oil in general, which are less
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28 dense than source-rock and tend to produce more water than gas fields.
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33 Operators are required to measure a major chemical used to formulate the well
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35 stimulation fluid as an indicator of hydraulic fracturing fluid in produced water.³² All operators
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37 using gel treatments chose total carbohydrate as an indicator chemical, since guar gum is used
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39 extensively in hydraulic fracturing.^{5, 15} Measurement of total carbohydrate in produced water
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41 apparently yielded a false positive result for guar. Total carbohydrate analysis is not a state
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43 certified or standard method and it hypothesized that the measurement of guar is subject to
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45 interference by chemicals present in oil or the presence of bacterial carbohydrates. Further
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47 studies are being conducted to establish standard protocols for the carbohydrate analysis in the
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49 context of measuring flowback and produced water quality monitoring.
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6. Declaration of Interest

Declarations of interest: none.

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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 (m³ m⁻¹)^c	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

^aMatrix acidizing treatment, ^bAcid fracturing treatment, ^cVolume of water used per length of well stimulation zone

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	47	8,000 ± 3,000	2,500 ± 500	50 ± 8
0520020	C/B	28	21 ± 5	26	16,000 ± 1,000	2,600 ± 300	100 ± 8
0520020	A/B	20	12 ± 0 ^d	13	4,300 ± 500	1,800 ± 500	30 ± 4
4320027	B/C	35	13 ± 2	36	6,500 ± 400	1,600 ± 200	30 ± 4
4320027	A/A	15	23 ± 1	31	12,000 ± 4,000	2,700 ± 300	50 ± 9

^aMean ± standard deviation

^bExcluding base fluid and proppant.

^cTotal number of individual constituents reported in the study period was 178 (including chemicals, proppants, and water).

^dAll stimulations used 12 chemicals each

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	Water sources and sample dates											
	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 as CaCO ₃	44	56	79	62	91	270	126	830	1,000	70	620	110
Alpha, pCi/L	1.66	< RDL	7.98	< RDL	2.74	< RDL	--	34.2	< RDL	< RDL	< RDL	14.9
Beta, pCi/L	--	< RDL	3.72	< RDL	2.59	< RDL	--	--	< RDL	< RDL	29.6	< RDL
Boron, mg/L	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	0.78	< RDL	< RDL	2.05	< RDL	< RDL	--	9.13	< RDL	3.29	< RDL	< RDL
Radium-228, pCi/L	< RDL	--	--	--	--	--	--	10.1	--	1.39	1.10	< RDL
Radon, pCi/L	--	--	< RDL	< RDL	--	< RDL	--	--	< RDL	--	--	--
Radon-222, pCi/L	--	< RDL	--	--	< RDL	--	--	50.8	--	96	--	--
TDS, mg/L	520	540	320	150	390	38,000	--	14,000	10,000	4,400	6,400	320
Uranium, pCi/L	< RDL	--	--	--	--	--	--	--	--	--	< RDL	12
Uranium, ug/L	--	--	--	--	--	--	--	--	--	--	--	18

Water used in Lost Hills (FAP 4320027) by: ^aProducer A (N=13), ^bProducer B (N=35), and ^cProducer A (N=2).

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 A). 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	N Initial	Mean Initial	SD Initial	N Final	Mean Final	SD Final	Paired	% change	Final < Initial
							Statistical		Final < Initial
							1=yes 0=no		= 1 Increase = 0 No change = 2
Alk (CaCO ₃)	440	2,000	1,000	441	2,900	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	2,000	476	200	400	1	-65	1
Br	475	110	60	476	120	40	1	14	0
Ca	475	7,000	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	3,000	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	3,000	476	200	100	1	-72	1

Analyte	N Initial	Mean Initial	SD Initial	N Final	Mean Final	SD Final	Paired	% change	Final < Initial
							Statistical		Final < Initial
							Different		= 1
							1=yes 0=no		Increase = 0
									No change =
									2
Li	475	30	60	476	7	3	1	-72	1
Mg	475	500	1,000	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	9,000	8,000	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	1,000	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	6,000	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

^aAll measurements were below limit of detection

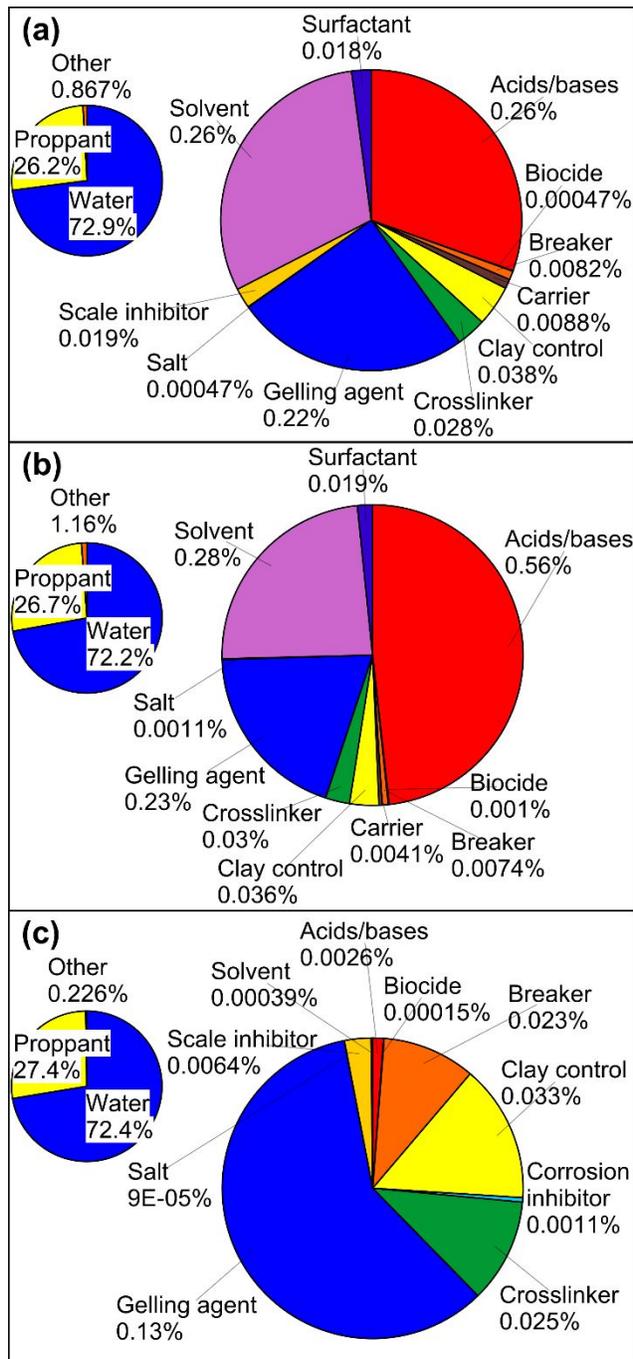


Figure 1. Relative mass fraction of total chemicals used (pie chart) and mean mass concentration (%) for hydraulic fracturing treatments conducted in the same geologic formation in the Lost Hills field (FAP 4320027). Formulations varied by several factors: (a) Service Company A using California Aqueduct water (N=13; TDS=520 mg L⁻¹); (b) Service Company A using produced water (N=2; TDS=6,600 mg L⁻¹); and (c) Service Company C using produced water (N=35; TDS=4,400 mg L⁻¹). Chemical additives were pooled by function according to Stringfellow *et al.* (2017)

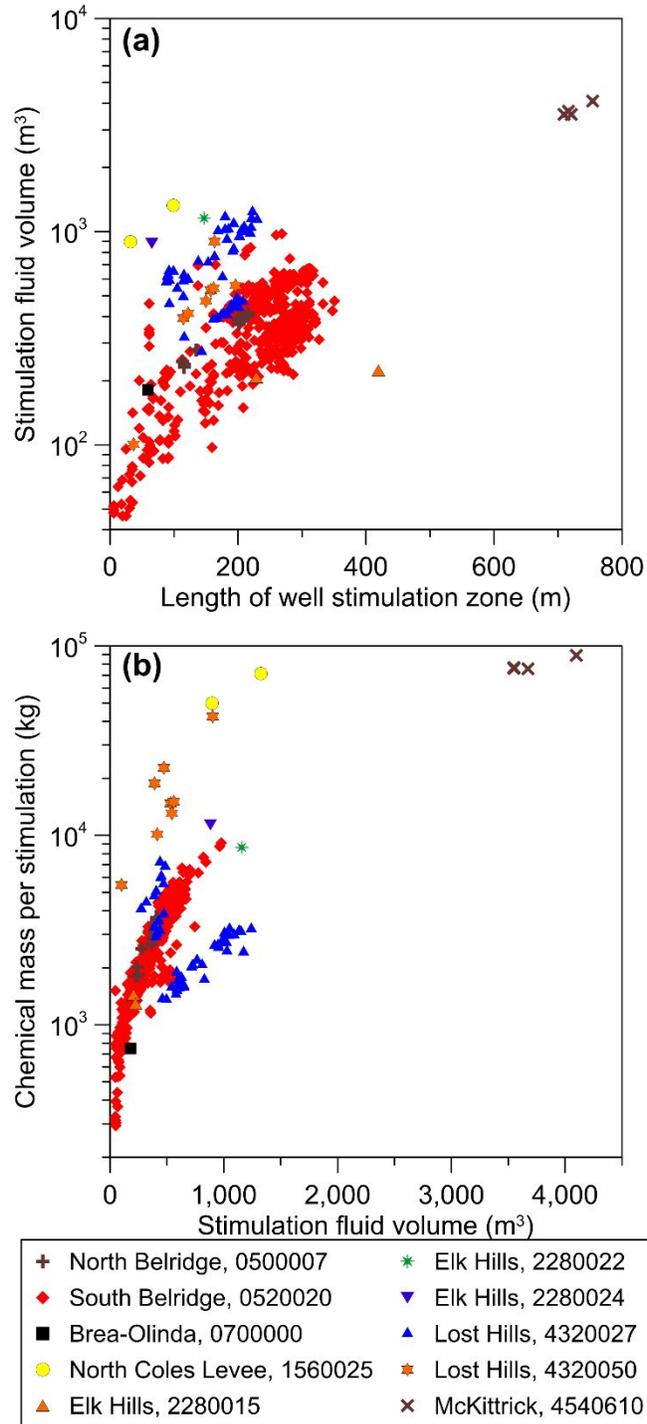


Figure 2. Relationship between: (a) hydraulic fracturing stimulation fluid volume and zone length, and (b) between chemical masses added to hydraulic fracturing stimulation fluid (excludes water and proppants) and fluid volume. Data are grouped by field-area-pool (FAP) code (N=616).

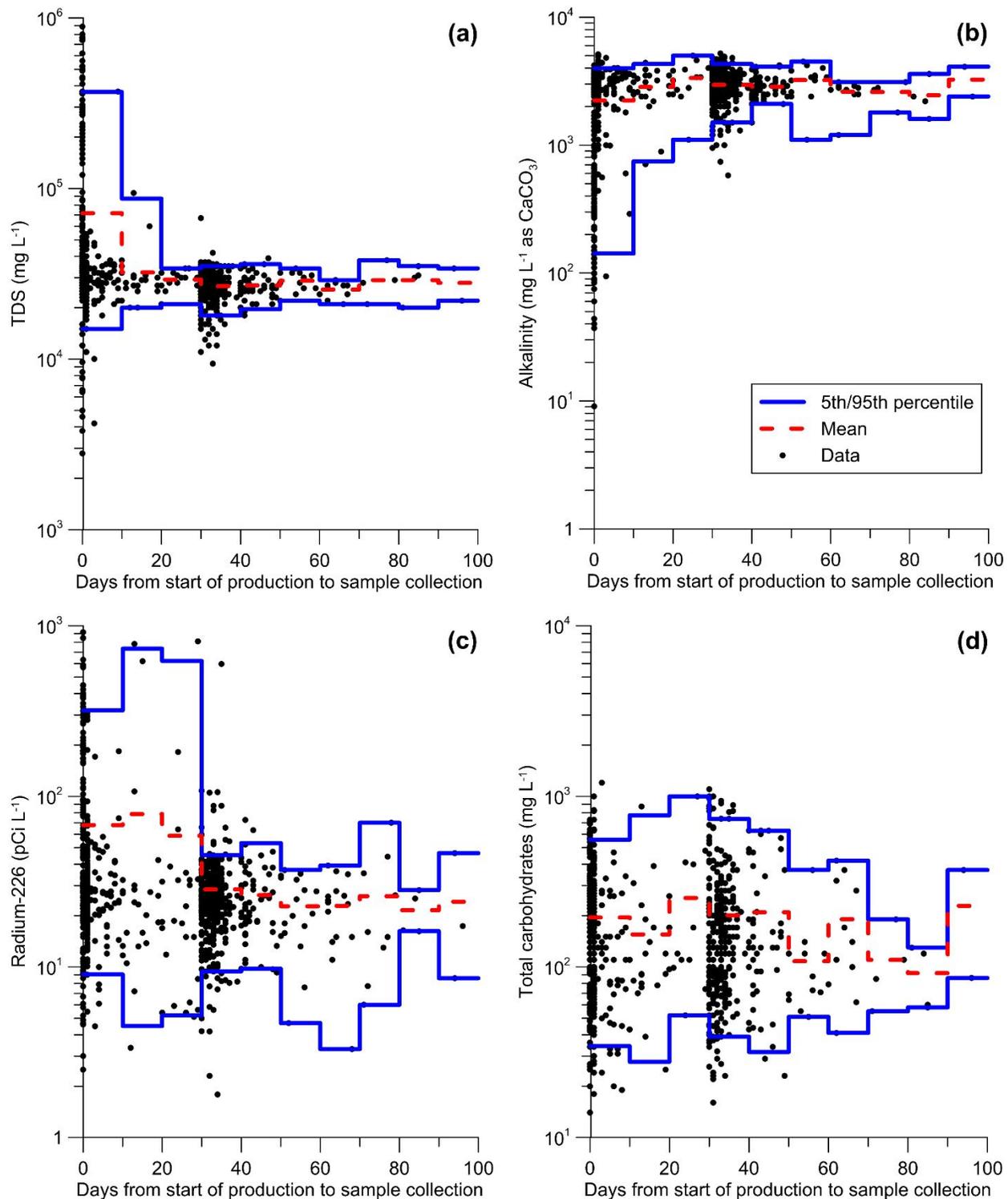


Figure 3. Recovered fluid water quality following hydraulic fracturing in the South Belridge field (FAP 0520020) with data shown for: (a) total dissolved solids (TDS), (b) alkalinity, (c) radium-226, and (d) total carbohydrates. Only radium-226 concentrations that were above the reported detection limit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

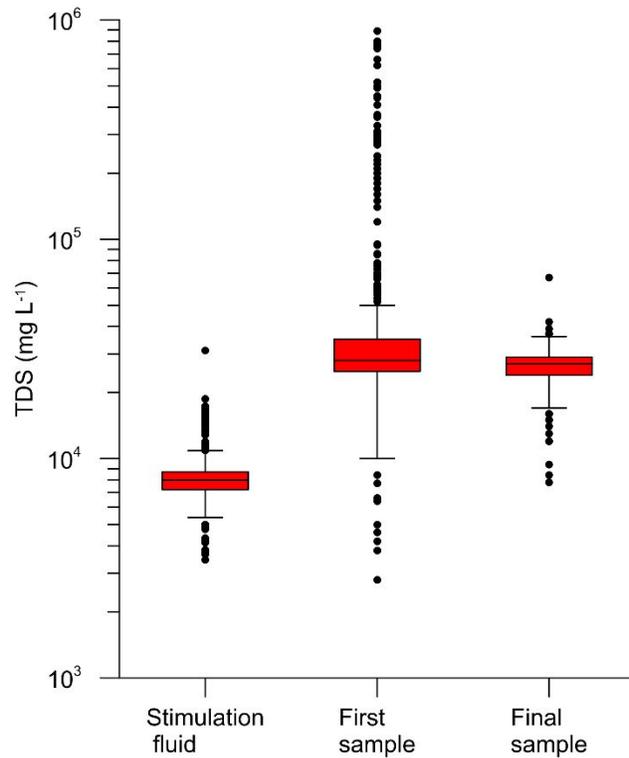
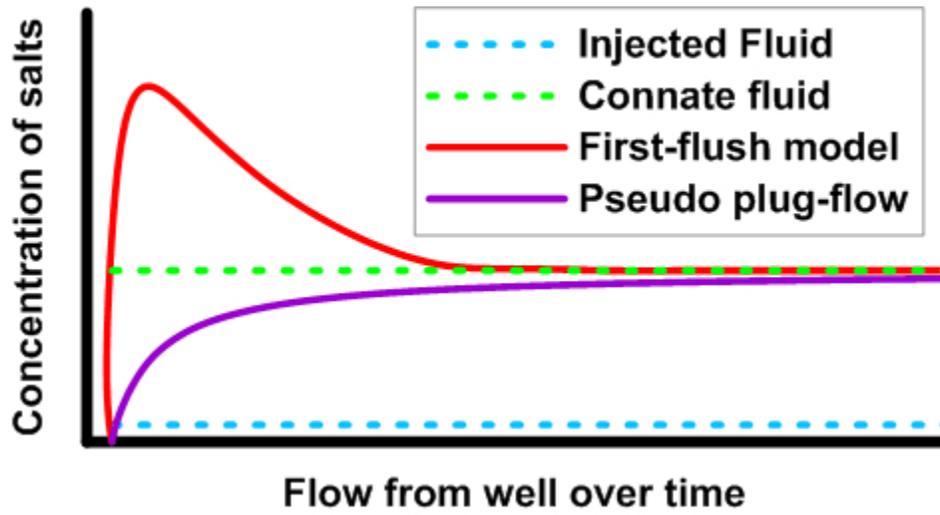


Figure 4. Comparison of total dissolved solids (TDS) calculated in the stimulation fluid and measured in the first and final samples recovered from wells undergoing hydraulic fracturing in the South Belridge field (FAP 0520020). The salinity of the injected fluid is significantly less than the salinity 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.

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