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Produced water geochemistry from hydraulically stimulated Niobrara Formation petroleum wells: Origin of salinity and temporal perspectives on treatment and reuse

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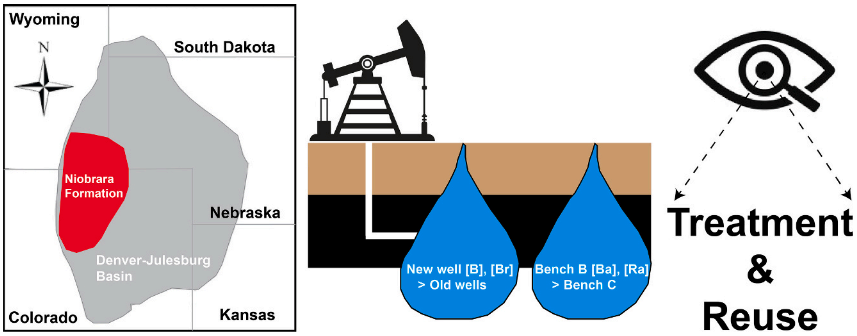
HIGHLIGHTS

- Boron is higher in new well fluids, likely due to injected crosslinking gels.
- Bromide is higher in new well fluids, likely due to injected brominated biocides.
- Barium and Ra fluid concentrations vary between benches of the Niobrara Formation.
- Na-Cl-Br systematics imply fluid salinity from diagenetically altered seawater.

GRAPHICAL ABSTRACT



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ABSTRACT

Produced water (i.e., a mixture of returned injection fluids and geologic formation brines) represents the largest volumetric waste stream associated with petroleum production in the United States. As such, produced water has been the focus of intense study with emphasis on understanding the geologic origin of the fluids, environmental impacts of unintended or intentional release, disposal concerns, and their commodity (e.g., lithium) potential. However, produced water geochemistry from many active petroleum plays remain poorly understood leading to knowledge gaps associated with the origin of brine salinity and parameters (e.g., radium levels) that can impact treatment, disposal, and possible reuse. Here we evaluate the major ion geochemistry, radium concentrations, and stable water isotope composition of ~120 produced water samples collected from 17 producing unconventional petroleum wells in Weld County, Colorado from the Late Cretaceous Niobrara Formation. This sample set encompasses eight produced water time series from four new wells across production days 0 to ~365 and from four established wells across production days ~1000 to ~1700. Additionally, produced water from nine

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other established Niobrara Formation wells were sampled at discrete time points ranging from day 458 to day 2256, as well as hydraulic fracturing input fluids. These results expand the available Niobrara Formation produced water geochemical data, previously limited to a few wells sampled within the first year of production, allowing for the heterogeneity of major ions and radium to be evaluated. Specific highlights include: (i) observations that boron and bromide concentrations are higher in produced waters from new wells compared to older, established wells, suggesting the role of input fluids contributing to fluid geochemistry; and (ii) barium and radium concentrations vary between the producing benches of the Niobrara Formation with implications for treating radiological hazards in produced waters from this formation. Furthermore, we explore the geochemical relationships between major ion ratios and stable water isotope composition to understand the origin of salinity in Niobrara Formation brines from the Denver-Julesburg Basin. These findings are discussed with perspective toward potential treatment and reuse of Niobrara produced water prior to disposal.

1. Introduction

Produced water is a term that refers to wastewater co-generated during oil and gas production and represents a major volumetric waste stream associated with petroleum production in the United States (Kondash et al., 2017; Scanlon et al., 2017). This wastewater is comprised of returned injection fluids mixed with geologic formation brines where the composition of the fluid varies between these two end members as a function of well age; i.e., produced water composition at early production times primarily represents returned injection fluids whilst fluids produced from older wells have compositions that represent deep basinal brines, or the natural formation water (e.g., Kharaka and Hanor, 2014; Rowan et al., 2015). Knowledge about the geochemical composition of produced water is necessary to predict the environmental impacts of unintended spills or leaks (e.g., Akob et al., 2016; Cozzarelli et al., 2017; Gallegos et al., 2021; Lauer et al., 2016; Mumford et al., 2020; Vengosh et al., 2014), understand human health issues associated with fluid exposure (e.g., Danforth et al., 2020; Danforth et al., 2019), to guide treatment strategies prior to reuse (Butkovskyi et al., 2017; Cooper et al., 2022; Dolan et al., 2018; McDevitt et al., 2020a, 2020b; Scanlon et al., 2020), and, increasingly, to identify cohosted critical mineral commodities (Darvari et al., 2024; Knierim et al., 2024; Mackey et al., 2024; Marza et al., 2024). Geochemical data from produced water also provides insight into geologic processes such as water entrainment during deposition (Kharaka and Hanor, 2014), diagenetic alteration (Land and Macpherson, 1992; Land and Prezbindowski, 1985; Moldovanyi and Walter, 1992), and fluid migration (e.g., Blondes et al., 2020; Engle et al., 2020; Warner et al., 2012) in petroleum reservoirs, increasing the collective understanding of important energy resources.

Despite the utility of produced water geochemical data, there are many active petroleum producing regions where these data are either missing, unavailable, or limited. This includes the Late Cretaceous Niobrara Formation in the Denver-Julesburg Basin which is currently (April 2024) producing ~700,000 barrels of oil per day and five trillion cubic feet of natural gas per day (U.S. Energy Information Administration, 2024). Niobrara Formation wells are typically hydraulically stimulated and are estimated to generate produced water volumes up to 18 million L per well over a well's lifetime (Kondash et al., 2017), although this estimate is almost a decade old. Available Niobrara Formation produced water geochemical data are mostly limited to studies evaluating fluids from only one to two wells, although one report sampled five wells (Caro, 2020), with samples typically collected within the first year of production (Esmaeilirad et al., 2015; Kim et al., 2016; Lester et al., 2015; Rosenblum et al., 2017a). Additionally, the majority of published Niobrara Formation produced water data are focused on organic (McDevitt et al., 2022; Rosenblum et al., 2017b) or biological (Amundson et al., 2023; Hull et al., 2018; Wang et al., 2019) components instead of the inorganic species that constitute the majority of the fluid's total dissolved constituents.

Here we expand the available geochemical data from Niobrara Formation produced water to include 119 samples collected from 17 wells starting from day 0 out to producing day 2256. This sample set includes time series from four new wells sampled from producing day 0 out to day ~365 and from four existing wells sampled from producing day ~1000 out to day ~1700. An additional nine existing wells were sampled at discrete, singular time points between producing days 458 to 2256. Also sampled were the fluids from two holding ponds used as input for hydraulic stimulation (i.e., injection fluid before chemical modification) and one fracking fluid (i.e., injection fluid after chemical modification). Wells producing from multiple benches of the Niobrara Formation are represented in the samples. Data include major ions (B, Ba, Br, Cl, Ca, Fe, K, Li, Mg, Mn, Na, Si, SO_4, Sr), total dissolved solids (TDS), specific gravity, radium isotopes (^{226}Ra and ^{228}Ra), and stable water isotope composition (δ^2H and δ^{18}O). These results allow for the evaluation of geochemical variation within the Niobrara Formation produced water samples as a function of geochemical parameter, production date, well age, and between production bench with perspective on treatment and reuse of the fluids. Furthermore, relationships between geochemical species (e.g., Ba and SO_4) impacting well treatment [e.g., scale formation (Tong et al., 2019)] are explored. Finally, compositional analysis (e.g., Engle and Rowan, 2013) of major ion geochemistry and stable water isotope composition interpretations allow for the origin of salinity in the Niobrara Formation brines to be constrained to diagenetically-altered evaporated seawater from the Late Cretaceous Western Interior Seaway (WIS).

2. Materials and methods

2.1. Samples

The Late Cretaceous Niobrara Formation in the Denver-Julesburg Basin consists of interbedded chalks and marls, termed benches (A, B, and C with C being the deepest), and was deposited from the Western Interior Basin during periods of peak flooding (Kauffman and Caldwell, 1993; Raynolds and Hagadorn, 2016; Sonnenberg, 2012). Depth and thickness of the Niobrara Formation benches varies across the basin, see Longman (2020) for a detailed discussion on the geology of the Niobrara Formation. Produced water samples were taken from a single operator's wells (name withheld) located in Weld County, Colorado, USA (Fig. S1) producing from either the B or C Bench of the Late Cretaceous Niobrara Formation. A total of 122 samples were acquired over several campaigns from October 2018 to November 2020; 65 from four new wells across production days 0 to ~365 (new well time series; NWTS), 45 from four established wells across production days 999 to 1776 (established well time series; EWTS), nine individual samples from nine established wells (EWs), and three injection fluids (two holding pond fluids and one fracking fluid) (Table 1**).** Samples were collected directly from the wellhead or separator following established protocols (Blondes et al., 2020; Engle et al., 2020) into triple-rinsed high-density polyethylene (HDPE) carboys. Sample conductivity and pH were measured on raw, unfiltered produced water using a Myron L 6PFC^E multimeter. The samples were then filtered to 0.45 μm (cellulose acetate filter) before being transferred into either glass amber bottles with no head space (δ^2H and δ^{18}O), soap-washed HDPE bottles (anions, Ra, TDS, and specific gravity), or acid-washed HDPE bottles (major cations) using a peristaltic

Table 1
Well ID, number of samples from each well, minimum and maximum time series sample point, and producing bench for the Niobrara Formation produced water samples.

Well ID	Number of samples	Min/max sampling day	Producing bench
EW-1	1	1259	B
EW-2	1	2256	B
EW-3	1	1259	B
EW-4	1	673	B
EW-5	1	1259	B
EW-6	1	1259	C
EW-7	1	1259	C
EW-8	1	458	C
EW-9	1	1431	C
EWTS-1	11	1002 / 1367	B
EWTS-2	12	999 / 1776	B
EWTS-3	11	1005 / 1370	C
EWTS-4	11	1012 / 1377	C
NWTS-1	15	0 / 367	B
NWTS-2	16	0 /368	B
NWTS-3	16	0 / 368	C
NWTS-4	18	0 / 367	C
FRACK FLUID	1	n/a	n/a
JMDJ INPUT FLUIDS POND 1	1	n/a	n/a
JMDJ INPUT FLUIDS POND 2	1	n/a	n/a

pump. Additionally, samples analyzed for major cations and Ra were acidified to a pH < 2 using trace-metal grade nitric acid. Samples were shipped on ice to the U.S. Geological Survey (USGS) laboratories in Reston, Virginia for analysis and were stored at ~3 °C prior to analysis.

2.2. Methods

Analytical methods used to determine major ion concentrations, TDS, specific gravity, and stable water isotope composition for all produced water samples have been previously described in detail (Blondes et al., 2020; Engle et al., 2020). Briefly, major cations (B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, Si, and Sr) concentrations were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) with a Horiba Ultima Expert following minimal dilution (dilution factor of 25). The use of ICP-OES for high salinity brines has been shown to be beneficial due to the salinity tolerance of the method compared to mass spectrometric approaches (Jubb et al., 2020). Major cation concentrations have a stated precision uncertainty $<\pm 2$ % at the 2σ level and a total estimated error of ±30 %. Anions (Br, Cl, and SO_4) were determined using ion chromatography via EPA Method 9056 A (U.S. Environmental Protection Agency, 2007) and have a stated precision uncertainty of ±5 % at the 2σ level and a total estimated error of ±15 %. Total estimated errors for major ions are based on recovery of matrix spikes. Mean charge balance for samples was ~ ± 2 % on a molar equivalence basis and typically was $<\pm 5$ % for individual samples. Specific gravity was determined by ASTM Method D—1429B (ASTM, 2013) and TDS was determined by EPA Method 160.1 (U.S. Environmental Protection Agency, 1999). Ra isotopes were measured at the USGS Naturally Occurring Radioactive Materials Laboratory (Reston, Virginia) using radiobarite, $(Ba,Ra)SO_4$, co-precipitation, and γ-ray spectrometry, following Kraemer (2005). Stable water $\delta^{18}O$ and $\delta^{2}H$ values were measured by dual-inlet isotope-ratio mass spectrometry at the USGS Reston Stable Isotope Laboratory (Reston, Virginia) following well-established protocols (Kendall and Coplen, 2001; Landwehr et al., 2014), and are presented relative to the Vienna Standard Mean Ocean Water (VSMOW) standard.

3. Results and discussion

3.1. Niobrara produced water heterogeneity

Data collected in this study allow for an evaluation of produced water compositional heterogeneity as a function of production day, well age, producing bench, and geochemical parameter (see Table 1). All sample data are given in Table S1 (Supporting Information) and in the associated USGS data release (Herzberg et al., 2024). Examination of TDS allows for major geochemical differences between samples to be rapidly observed, and this parameter is also a key consideration for treatment and potential reuse of these fluids (Ahmadun et al., 2009; Cooper et al., 2022). With this perspective, the TDS level in all samples is <35,000 mg/L, approximately equivalent to that of modern seawater. This relative freshness [e.g., Appalachian Basin produced waters have TDS values approaching ~300,000 mg/L (Blondes et al., 2020)] makes potential reuse of Niobrara Formation waters for future hydraulic stimulation (Lester et al., 2015), irrigation (Dolan et al., 2018), or stream augmentation (Cooper et al., 2022; McDevitt et al., 2020b) attractive, as opposed to other uses, such as dust suppression (Tasker et al., 2018).

In the samples from the four wells corresponding to the new well time series (NWTS; collected days 0 to ~365 post initial production), TDS levels vs. production day (Fig. 1) indicate that the gross geochemical composition of the samples approaches approximate steady state by production day 200. The exception to this is NWTS-4 which shows slightly decreasing TDS values post day 200, potentially indicating the input of fresh condensate water (Molofsky et al., 2023). TDS values at day 200 range from 22,800 mg/L (NWTS-1) to 26,500 mg/L (NWTS-2) (Table S1, Fig. 1B). Note that the TDS levels of the input fluids are all <2000 mg/L, such that injection of these fluids cannot explain the TDS values observed for the Niobrara produced water samples. The approach of produced water TDS to steady state in Denver-Julesburg samples shares similarities with behavior of produced water samples in the Marcellus Shale (Rowan et al., 2015), which reach approximate steady state after ~200 days in production. Further, prior observations from the Niobrara Formation show steadily increasing TDS out to production day ~200, although this time point represented the final sampling point of previous work (Kim et al., 2016; Rosenblum et al., 2017a). Additionally, TDS levels for the NWTS samples are not distinct when comparing the producing B and C benches. Fluids produced from Bench B (i.e., NWTS-1 and NWTS-2, Table 1) at day ~365 have TDS levels which differ by 4400 mg/L (~20 %). Similar well-level differences in TDS values are observed when comparing samples collected from Bench C (i.e., NWTS-3 and NWTS-4) (Table S1). This indicates that there is limited reservoir interconnectivity, as expected given the low permeabilities of the Niobrara Formation (Pollastro and Scholle, 1986), and that there is no benefit to targeting produced water from either the B or C Bench when considering TDS levels for treatment prior to potential reuse.

Evaluation of produced water TDS levels for established wells (EWs) measured at discrete time points and for the four established well time series (EWTS; collected days ~1000 to ~1700 post initial production) exhibit high TDS variability across samples, with TDS levels ranging from 17,000 mg/L (EWTS-1, day 1302) to 33,000 mg/L (EWTS-4, day 1264) (Fig. 1A, Table S1). This variability is driven, in part, by on-going well treatments. For example, all four EWTS wells were treated with a biocide to prevent H_2S formation around production day 1000. The introduction of such treatment fluids can dilute the well produced water, although in this case samples were not acquired for ~2 weeks following the well treatment and the TDS values had recovered to approximately the mean values by day ~1020. It is important to highlight that recently treated wells are typically avoided during produced water sampling campaigns. This built-in sampling bias is driven by study hypotheses seeking to address questions related to the geologic origin of reservoir fluids or understand the potential resource levels in produced waters, both of which would be impacted by on-going or recent well treatments. However, from a treatment and reuse perspective, data showing that produced water geochemistry can be highly variable years into production provides insight for guiding treatment technologies and the timing of potential reuse. For example, EWTS-4 produced waters have TDS values that range from 26,500 mg/L (day 1071) to 33,000 mg/L (day 1264). Given that the TDS values for EWTS-4 at day 1071 match prior reports for the Niobrara Formation at production day ~200, in the absence of the data shown here, it would be reasonable, albeit incorrect, to assume that this TDS value would be relatively static given the age of the well.

While TDS provides coarse insight into produced water geochemistry, evaluating the individual major ions present in the samples allows for more nuanced interpretations. All major ions are shown as a function of production day (Fig. S2, Supporting Information) and as a function of TDS (Fig. S3, Supporting Information). Produced water data for four major ion components (Na, B, Ba, and Br) that have relevance for treatment and potential reuse are displayed as a function of TDS in Fig. 2. Na content of the produced water samples correlates strongly ($R^2 = 0.98$) with TDS levels (Fig. 2A) and displays little variation as a function of well age (i.e., new and established wells fall on same trend) or production bench. This is similar to observations for Cl and is expected as Na and Cl make up >80 % of the TDS for the majority of samples. As one of the major components of produced water salinity, Na is a focus of treatment prior to reuse (Ahmadun et al., 2009) and has been shown to accumulate in soils and surface waters exposed to untreated produced waters following spills, dumps, or unintended release (Adams, 2011; Akob et al., 2016; Skalak et al., 2014).

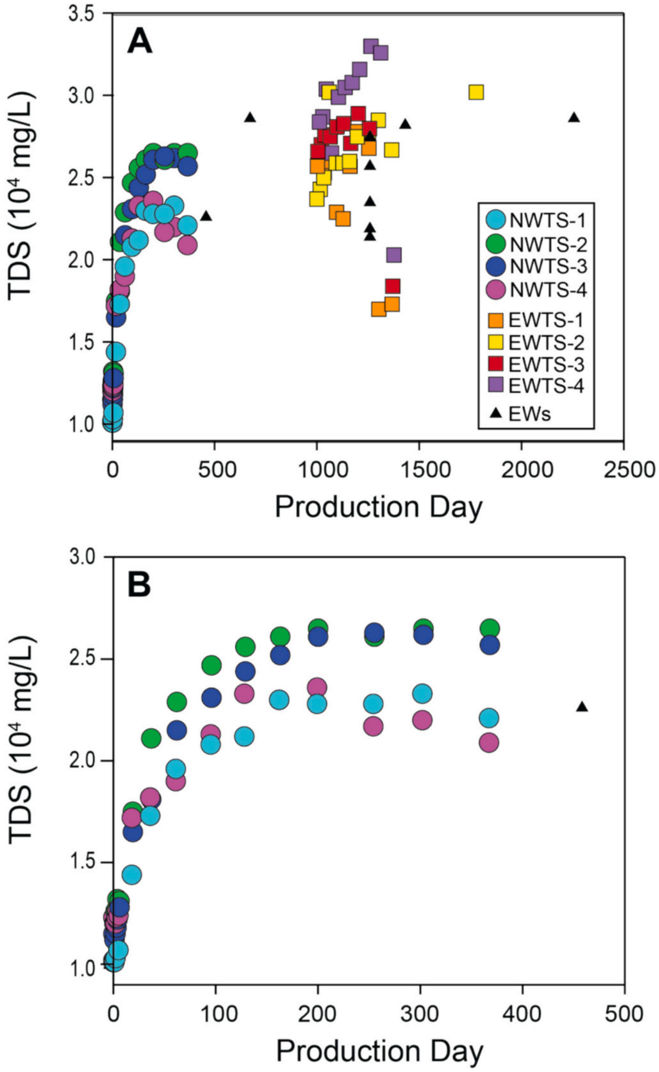

Fig. 1. Total dissolved solids (TDS) vs production day for the Niobrara Formation produced water samples. New well time series (NWTS, circles), Existing well time series (EWTS, squares), Existing wells (EW, triangles). A) TDS data for all samples out to producing day 2500. B) TDS data out to producing day 500 corresponding to the four NWTS and one EW. Legend in panel A corresponds to both panels.

Similar to Na, elevated B has been found in environments impacted by both unintentional produced water release (Cozzarelli et al., 2017) and reuse for irrigation (Kondash et al., 2020). Produced water B concentrations also have utility as a tracer of clay mineral diagenesis and marine kerogen breakdown (Engle et al., 2016; Kharaka and Hanor, 2014; Williams et al., 2015). In contrast to Na concentrations, here B levels are largely invariant with TDS (Fig. 2B) and/or production day (Supporting Information, Fig. S3), and are greater for all NWTS samples than found in any sample from an existing well (i.e., EWTS or EW). This signal (i.e., $[B]_{NWTS} > [B]_{EWTS}$ for all wells) presumably indicates the use of borated gel crosslinkers in the hydraulic fracturing fluid formulation (Li et al., 2016), during completion of the four wells comprising the NWTS sample set, although B concentration was below detection (<30 μg/L) in the one fracking fluid collected. Somewhat surprisingly, the B content of the NWTS samples is still elevated over EWTS levels out to production day ~365, indicating the possible persistence of B input from gel crosslinkers. Taken together, observations on the B content of the Niobrara produced waters indicate that treatment strategies prioritizing lower salinity produced waters (e.g., NWTS samples) may have to simultaneously treat elevated levels of B, a relatively small, diffuse ion. Moreover, caution is warranted when applying B isotopes from hydraulically stimulated reservoirs for geologic interpretations as these signals may be compromised by persistent artifacts from input fluids.

The other two major ions highlighted in Fig. 2, Ba (Fig. 2C) and Br (Fig. 2D), exhibit bimodal behavior when plotted against TDS. For Ba there is a clear distinction between Bench B and Bench C samples where Bench B fluids have up to ~40 % more Ba than those produced from Bench C for TDS levels >20,000 mg/L (representing fluids not dominated by early flowback). This difference has important consequences for scale formation [specifically barite ($BaSO_4$) formation] and associated Ra hazards, as discussed in the following section. In contrast to Ba, the differences observed in Br content as a function of TDS appear between fluids from new vs. established wells. The reasons for this difference are unclear although the use of brominated biocides [e.g., 2,2-dibromo-3-nitriloproppionamide (CAS 10222–01-2)] used to prevent H_2S formation are a likely reason for this difference. For example, on production day ~1000 all four EWTS wells were treated for H_2S, as discussed above, and the Br concentrations for the EWTS produced water samples from this day are generally higher (Fig. S2) than for other samples from these wells. Furthermore, in the FracFocus database (https://www.fracfocus.org) there are currently (June 2024) 14,456 wells in Weld County, Colorado with fracking fluid compositions provided. Of these wells, 2472 (~17 %) have 2,2-dibromo-3-nitriloproppionamide listed as an ingredient, demonstrating the wide use of brominated compounds during petroleum production. While Br does not pose specific treatment challenges, it can form toxic organo-bromine byproducts during chlorination of drinking water sources (Harkness et al., 2015; Huang and Zhang, 2020; Parker et al., 2014) and 2,2-dibromo-3-nitriloproppionamide itself has been shown to impact stream microbial communities following produced water discharges (Akob et al., 2021). As such, the Br data shown in Fig. 2D indicate that Niobrara produced waters from newer wells in the Denver-Julesburg Basin may represent greater risks in the case of unintended release prior to treatment than fluids from more established Niobrara Formation wells.

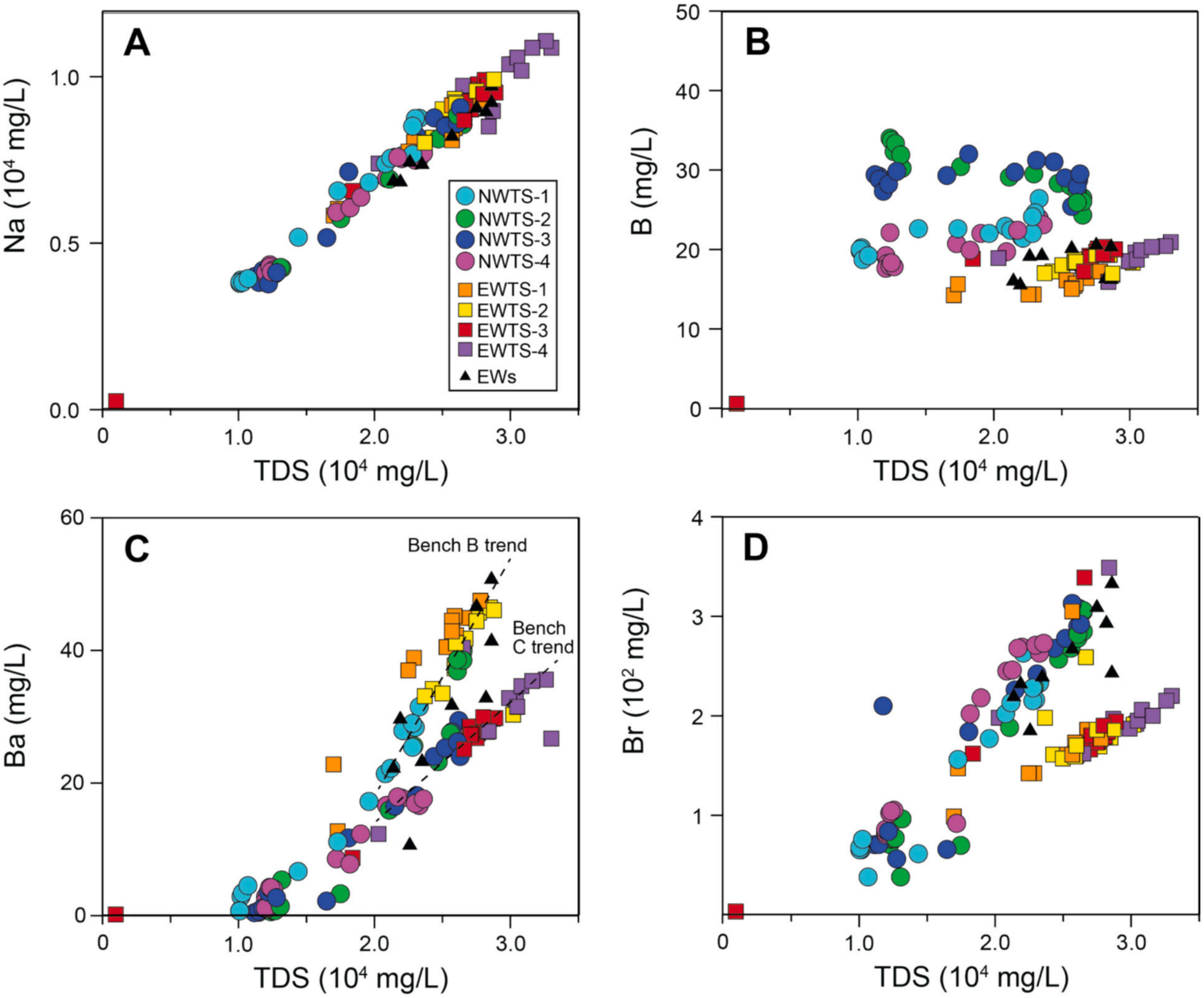

Fig. 2. Sodium (Na), boron (B), barium (Ba), and bromide (Br) concentrations vs total dissolved solids (TDS) for the Niobrara Formation produced water samples. New well time series (NWTS, circles), Existing well time series (EWTS, squares), Existing wells (EW, triangles). Legend in panel A same for panels B, C, and D. Dashed lines in panel C represent general trends between Bench B and C data.

3.2. Scale formation and radium hazards

Produced water contains constituents that can precipitate as mineral scale under certain conditions and constrict the wellbore (Lester et al., 2015) or clog membranes used for treatment (Tong et al., 2019). As such, fracking fluid recipes may contain scale inhibitors (e.g., ethylene glycol or polymaleic acid) to reduce scale formation, deposition, or particle size in order to maintain well productivity (He and Vidic, 2016). Specifically, barite formation is a concern during hydraulic stimulation and early flowback when SO_4-rich input fluids mix with Ba-rich formation brines. While other alkaline earth metals (e.g., Ca and Sr) present in formation brines can also form sulfate scalant minerals [e.g., gypsum ($CaSO_4.2H_2O$) or celestine ($SrSO_4$)], the formation of barite is kinetically favorable under the geochemical conditions present in most petroleum reservoirs (Hina and Nancollas, 2000; Zhang et al., 2019). Examining Ba and SO_4 in the produced water samples and input fluids considered here (Fig. 3A) demonstrates the inverse relationship between these constituents where waters high in SO_4 (>100 mg/L, input fluids) have negligible Ba content. That is, the dominant source of SO_4 in these wells is the injected fluids during hydraulic stimulation and/or well treatments. Further reinforcing this point, SO_4 concentrations decreases with production age for NWTS wells and is generally lower in EWTS well fluids than NWTS wells (Fig. S2). Ba content becomes appreciable for produced water samples when [SO_4] <100 mg/L and, in this regime, there are two scenarios with increasing Ba concentrations. The first scenario involves SO_4 levels decreasing to below the practical quantification limit (<0.75 mg/L) with increasing Ba, as expected for fluids where barite precipitation is controlling the Ba and SO_4 concentrations in solution. This is the case for the majority of the EWTS wells and for NWTS-1. Alternatively, for NWTS-2, NWTS-3, NWTS-4, and several EW samples, the SO_4 content converges to ~40 mg/L as Ba concentration increases (Fig. 3A). This observation suggests the presence of some buffering species, potentially an injected scale inhibitor, keeping Ba in solution at appreciable SO_4 concentrations.

Examination of the Ba/SO_4 molar ratio as a function of production day (Fig. 3B) provides a temporal perspective of these two scenarios. The Ba/SO_4 molar ratio in the samples spans almost five orders of magnitude with produced waters from early production times for the NWTS samples exhibiting low values indicative of relatively high SO_4 concentrations. As production day increases, so does the Ba/SO_4 molar ratio for the NWTS samples until a threshold value of ~1 is reached. At that point the Ba/SO_4 molar ratio becomes largely invariant with time out to the last sampling point of ~365 days, except for NWTS-1. For NWTS-1 the Ba/SO_4 molar ratio continues to increase with production time and looks similar to the results for the EWTS samples. The Ba/SO_4 molar ratio vs. production day results strongly suggest some persistent buffering species have been added to wells NWTS-2, NWTS-3, and NWTS-4, which prevents barite formation (and the concomitant increase in the Ba/SO_4

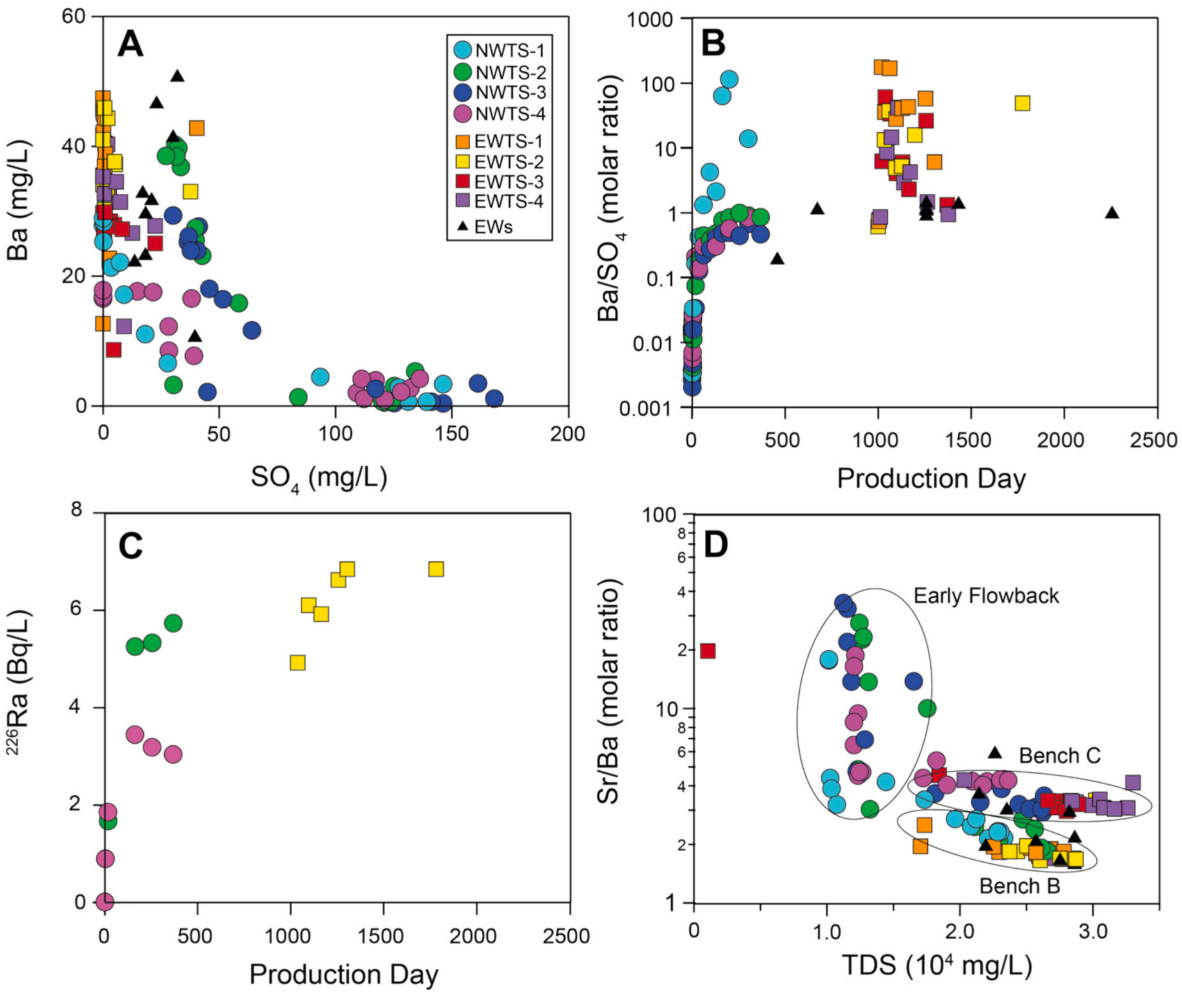

Fig. 3. A) Barium (Ba) vs. sulfate (SO_4) concentrations in mg/L for all produced water samples. B) Ba/SO_4 molar ratio vs production day for all produced water samples. C) ^{226}Radium concentration in Bq/L vs production day for three wells, New well time series (NWTS-2, green circles), NWTS-4 (pink circles), and Existing well time series (EWTS-2, yellow squares). D) Sr/Ba molar ratio vs production day for all produced water samples. Circled data correspond to samples dominated by early flowback and originating from Bench C and B. Legend in panel A same for all panels.

ratio) whereas no buffering species has been added to NWTS-1. Furthermore, as the data for the single time point sampled EW wells also does not show Ba/SO_4 molar ratios >1, this may also suggest the pervasive use of scale inhibitors within Niobrara Formation wells during production, and not just for newly completed wells.

Radiological hazards in produced waters generally consist of the two long-lived, readily soluble isotopes of Ra, ^{226}Ra and ^{228}Ra (e.g., Rowan et al., 2015; Rowan et al., 2011). In the Denver-Julesburg Basin, Rosenblum et al. (2017a) showed that ^{226}Ra content was ~2 orders of magnitude higher than other naturally occurring radioactive materials (NORM) in fluids from a single well. Ra-content of produced waters is often discussed alongside sulfate-mineral formation due to the propensity of Ra to preferentially incorporate into barite to form radiobarite (Kondash et al., 2014; McDevitt et al., 2020a). Here, both ^{226}Ra and ^{228}Ra levels were measured for a select suite of samples from NWTS-2 (Bench B), NWTS-4 (Bench C), EWTS-2 (Bench B), and the input fluids (Fig. 3C, Table S1, Supporting Information). Although the Niobrara Formation produced waters studied here show appreciable ^{226}Ra (up to ~7 Bq/L), this is approximately 20× lower than more saline oilfield waters such as the those from the Marcellus Shale (Rowan et al., 2015). Both ^{226}Ra and ^{228}Ra were below detection for the input fluids and ^{228}Ra was below the detection limit for all samples, implying that rock ^{238}U concentrations are greater than ^{232}Th levels in both the Niobrara Formation Bench B and C (Kraemer and Reid, 1984). For NWTS-2 and NWTS-4, ^{226}Ra concentrations increase with production age until an approximate steady state (within ±10 %) is reached around day ~160. Prior to day ~160, Ra is lowered both from dilution with input fluids and removal in the subsurface by radiobarite precipitation, evident by the lower Ra concentrations during early production relative to the steady state concentrations (e.g., NWTS-2 production day 18 ^{226}Ra concentration is ~30 % of steady state concentration) compared to the relative concentrations of conservative major ions (e.g., Na and Cl, ~65 % and ~ 61 % of steady state concentration respectively) at the same time points.

Bench B Niobrara Formation produced waters have higher (by ~30 %) ^{226}Ra concentrations compared to Bench C produced water (Fig. 3C), indicating these fluids represent greater NORM hazards of the two producing intervals evaluated here. However, this situation is somewhat mitigated by higher Ba levels observed for Bench B produced waters (Fig. 2C), implying that more Ra will be removed via radiobarite precipitation during early flowback for Bench B produced waters than in fluids produced from Bench C. Furthermore, prior observations by McDevitt et al. (2020a) link Ra incorporation into precipitated sulfate-minerals in produced waters to the Sr/Ba molar ratio present where higher Sr/Ba molar ratios resulted in more efficient Ra removal. Here, if samples impacted by early flowback are discounted, the Sr/Ba molar ratio in the produced waters varies by producing bench (Fig. 3D). Bench C produced waters have Sr/Ba molar ratios ~4 whereas Bench B samples have Sr/Ba molar ratios closer to ~2. This difference suggests Ra removal from Bench B fluids via radiobarite precipitation will be less efficient than removal from Bench C fluids. The complex interplay between Ra content and scale forming species (i.e., Ba and Sr) highlight that the optimal treatment for Ra removal from Niobrara Formation produced water may depend on the production bench from which the fluids originate.

3.3. Origin of Niobrara Formation brine salinity

Limited information is available on the geologic origin of salinity in formation brines from the Niobrara Formation in the Denver-Julesburg Basin. Prior work discussing this topic concluded that salinity in these fluids originated from evaporated paleo-seawater diluted with injected fresh water used for hydraulic stimulation (Rosenblum et al., 2017a), with limited discussion on geologic origin. While understanding the geologic origin of salinity in formation brines from the Niobrara Formation may not inform treatment strategies and/or potential reuse perspectives, the sample suite and data set presented in this study present a unique opportunity to evaluate the geologic origin of the fluids. However, a word of caution is warranted prior to this discussion, given the influence of input fluids on the produced water geochemistry in the dataset. This influence is most pronounced for the NWTS samples, and as such, evaluation of the geologic origin of produced water salinity is restricted to samples from established wells (both time series and single point sampled wells) that were not taken immediately following well treatment.

The origin of salinity in formation brines is typically dominated by two processes: (i) evaporation of entrained seawater and/or (ii) halite dissolution by fresh meteoric water inputs (Kharaka and Hanor, 2014). A third process involving the redissolution of halite by evaporitic brines, so-called halite recycling, has also been demonstrated to be an important mechanism for salinity enrichment (Engle et al., 2020; Knauth and Beeunas, 1986). These processes can be modeled from a starting seawater composition and are typically analyzed by considering molar ratios involving Na, Cl, and Br. The use of isomeric log ratio (ilr)-plots, instead of direct ratios, for this purpose has been shown to avoid spurious numerical correlations (Engle and Rowan, 2013), and this approach is adopted here.

The Niobrara Formation was deposited during the Late Cretaceous on the western margin of the WIS, and as such, the major ion geochemistry of formation fluids should reflect the major ion geochemistry of Cretaceous seawater (Timofeeff et al., 2006). There is some evidence that the salinity of the WIS was significantly lower than unrestricted Cretaceous marine settings and modern seawater (Petersen et al., 2016), and this could explain, in part, the relative freshness of produced water in the Niobrara Formation. Examining the ilr-transformed produced water Na-Cl-Br data (Fig. 4) indicate that the samples from this study and from Rosenblum et al. (2017a) plot largely along the halite recycling path, while the single data point from Lester et al. (2015) plots along the seawater evaporation path. Stratigraphically, the only major evaporite beds within the Denver-Julesburg Basin are of Permian age (Raynolds and Hagadorn, 2016), although there is limited evidence that suggests Permian salt dissolution and transport impacted Cretaceous-level structures (Oldham, 1997). Alternatively, Br inputs from kerogen breakdown during catagenesis (e.g., Engle et al., 2016) may also explain the ilr-transformed data given the relative low salinities in the Niobrara Formation. Indeed, relatively low

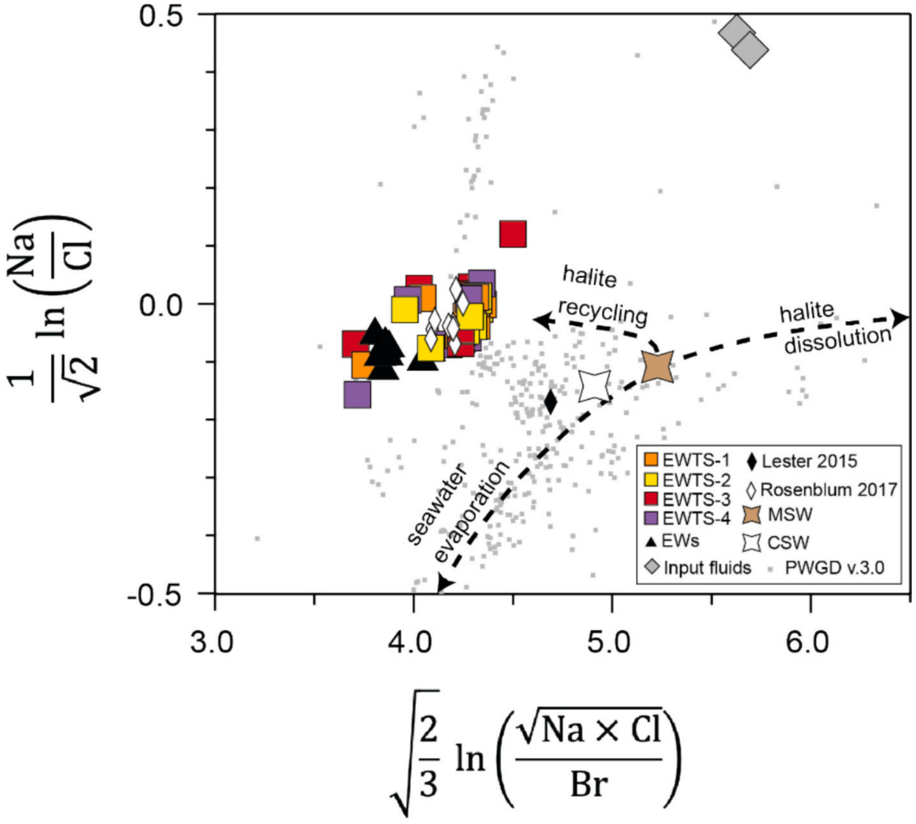

Fig. 4. Sodium-Calcium-Bromide (Na-Cl-Br) isomeric log ratio (ilr)-plot based on Engle and Rowan (2013) with halite recycling field taken from Engle et al. (2020). Produced water data from this study (squares and triangles), input fluids (grey diamonds), data from Rosenblum et al. (2017a) (white diamonds) and Lester et al. (2015) (black diamond), values from modern seawater (MSW, tan star) and Cretaceous seawater (CSW, white star), and data (n = 366, grey dots) from the U.S. Geological Survey National Produced Waters Geochemical Database (PWGD) (Blondes et al., 2023) for Cretaceous-aged formations filtered for [Br] > 10 mg/L and [Cl] > 1000 mg/L. CSW values based on concentrations from Timofeeff et al. (2006).

salinity formation brines are more susceptible to diagenetic alteration (e.g., kerogen breakdown, albitization, etc.) than higher-salinity fluids where evaporation/salt dissolution processes dominate. Given the relatively low salinity of the Niobrara Formation produced waters evaluated here (<35,000 mg/L TDS) we suggest diagenetic alteration is a more likely source of the observed salinity patterns than halite dissolution and/or recycling.

Finally, stable water isotope composition for the produced water samples and the input fluids are shown in Figs. 5A and B. The water isotope data generally plot below the local meteoric water line for Colorado (CO LMWL) and demonstrate expected trends from mixing fresh surface water with isolated brines (e.g., Blondes et al., 2020) as a function of production day. That is, fluids from NWTS wells are generally mixtures with a greater component of input fluids than fluids from established wells (both EW and EWTS), and, as such, plot closer to the input fluid values than produced water from established wells. Few differences in the water isotope ratios are observed between the producing benches for samples from new wells. However, data from established wells indicate the produced water from Bench C is heavier (less negative $\delta^{18}O$ values) than fluids from Bench B, consistent with the higher temperatures in the deeper Bench C. Ultimately the water isotope data provides further evidence that the Niobrara Formation produced waters do not originate as modern meteoric water, but instead are consistent with isolated deep brines.

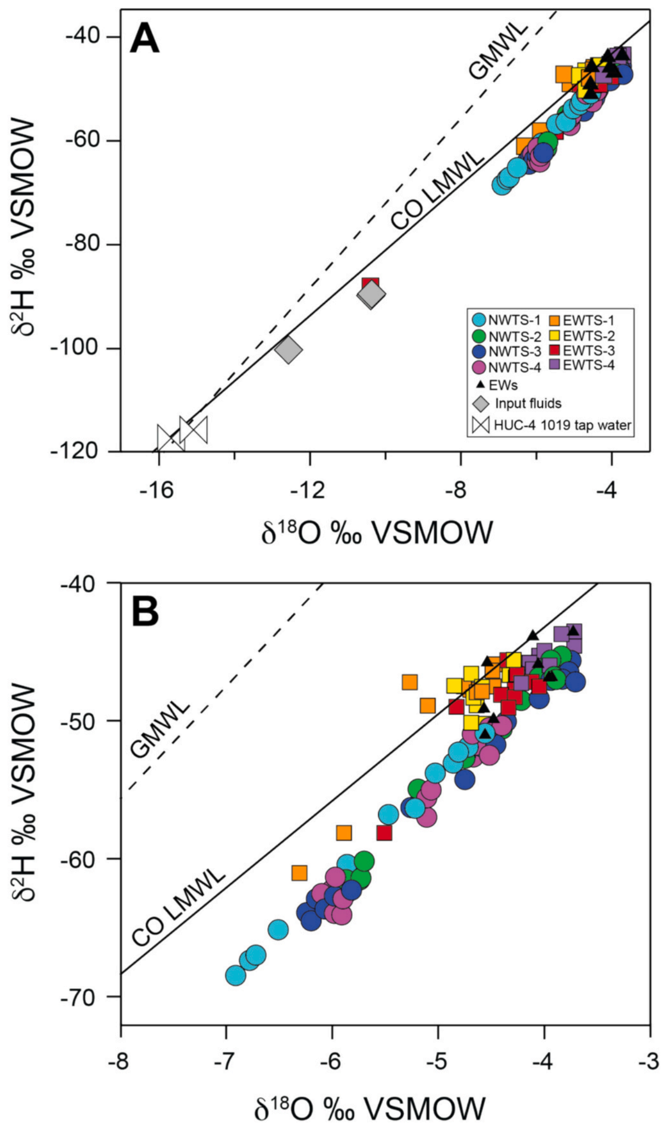

Fig. 5. A) Stable water isotope compositions relative to Vienna Standard Mean Ocean Water (VSMOW, δ^2H vs δ^{18}O) of the produced water samples (circles, squares, and triangles), input fluids (grey diamonds), and northern Colorado tap water (white bowties). Dashed trace represents the global meteoric water line (GMWL) and solid trace is the local meteoric water line (LMWL) for Colorado and are taken from Kendall and Coplen (2001). Tap water values taken from Landwehr et al. (2014). B) Same as panel A, zoomed in on produced water data field. Legend same for panels A and B.

4. Conclusions

Major ion geochemistry and water isotope data are presented for 119 produced water samples from 17 unconventional petroleum wells from the Late Cretaceous Niobrara Formation in the Denver-Julesburg Basin. Samples include time series from four new wells, from production day 0 to ~365, time series from four existing wells, from production day ~1000 to day ~1700, and nine single time points from nine existing wells. This dataset greatly expands the available information on produced water geochemistry from the Niobrara Formation, an important, actively producing petroleum play. Data indicate that the geochemical composition of Niobrara Formation produced water is highly variable, even after initial flowback has ended, driven in part by ongoing well treatments throughout the lifetime of a producing well. This variability has important implications for treatment strategies and the potential reuse of these fluids. Other key findings include:

1) Boron levels are higher in produced waters from new wells, presumably due to injected B-containing crosslinking gels, indicating that treatment strategies targeting lower salinity fluids (i.e., those during early production days) will have greater B levels to address.
2) Bromide concentrations are higher in produced waters from new wells. A potential source of this variation is the injection of brominated biocides. This finding signifies that fluids from new wells can carry a greater risk for toxic organo-bromide production than produced waters from established wells if they are mixed with freshwaters that undergo disinfection treatment.
3) Barium and Ra concentrations vary between the producing benches of the Niobrara Formation with produced waters produced from Bench B having higher NORM hazards due to higher Ra concentrations although complex interactions with scale forming ions (i.e., Ba and Sr) complicate potential treatments.
4) Isomeric log ratio (ilr)-analysis of Na-Cl-Br systematics suggest that the produced water salinities in the Niobrara Formation most likely originate as diagenetically altered Cretaceous seawater while stable water isotope compositions confirm that these fluids did not originate from modern meteoric water input.

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CRediT authorship contribution statement

Aaron M. Jubb: Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Formal analysis, Data curation. **Jenna L. Shelton:** Writing – review & editing, Conceptualization. **Bonnie McDevitt:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Kaela K. Amundson:** Writing – review & editing, Methodology. **Amanda S. Herzberg:** Writing – review & editing, Data curation. **Jessica Chenault:** Writing – review & editing, Methodology, Formal analysis. **Andrew L. Masterson:** Writing – review & editing. **Matthew S. Varonka:** Writing – review & editing, Methodology. **Glenn Jolly:** Writing – review & editing, Methodology, Data curation. **Christina A. DeVera:** Writing – review & editing, Investigation. **Elliott Barnhart:** Writing – review & editing, Investigation. **Michael J. Wilkins:** Writing – review & editing. **Madalyn S. Blondes:** Writing – review & editing, Project administration, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data available in associated USGS data release: https://doi.org/10.5066/P14CRSQQ

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