

## Review

## Fit-for-purpose treatment goals for produced waters in shale oil and gas fields

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## ABSTRACT

Hydraulic fracturing (HF), or “fracking,” is the driving force behind the “shale gas revolution,” completely transforming the United States energy industry over the last two decades. HF requires that 4–6 million gallons per well (15,000–23,000 m<sup>3</sup>/well) of water be pumped underground to stimulate the release of entrapped hydrocarbons from unconventional (*i.e.*, shale or carbonate) formations. Estimated U.S. produced water volumes exceed 150 billion gallons/year across the industry from unconventional wells alone and are projected to grow for at least another two decades. Concerns over the environmental impact from accidental or incidental release of produced water from HF wells (“U-PW”), along with evolving regulatory and economic drivers, has spurred great interest in technological innovation to enhance U-PW recycling and reuse. In this review, we analyze U-PW quantity and composition based on the latest U.S. Geographical Survey data, identify key contamination metrics useful in tracking water quality improvement in the context of HF operations, and suggest “fit-for-purpose treatment” to enhance cost-effective regulatory compliance, water recovery/reuse, and resource valorization. Drawing on industrial practice and technoeconomic constraints, we further assess the challenges associated with U-PW treatment for onshore U.S. operations. Presented are opportunities for targeted end-uses of treated U-PW. We highlight emerging technologies that may enhance cost-effective U-PW management as HF activities grow and evolve in the coming decades.

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## 1. Introduction

The water footprint of oil and gas (O&G) production relevant to unconventional gas and tight oil (UGTO) recovery has received considerable attention in recent years, though nation-wide reviews on the topic remain scarce (Kondash and Vengosh, 2015; Kondash et al., 2018). Hydraulic fracturing (HF), or “fracking”, is the predominant well stimulation method used in the United States for UGTO recovery from shale and carbonate reservoirs (U.S. EPA, 2016a). During HF operations, a water-based fluid (fracking/fracturing fluid) is injected into hydrocarbon-bearing deposits at pressures sufficient to crack (or fracture) the formation. During production, large quantities of water are generated alongside the recovered UGTO (typical water-to-oil ratio ~3:1). Many O&G companies have great interest in reusing this water for additional HF operations to improve their water footprint (*i.e.*, minimize freshwater withdrawals and potential impacts upon disposal) and to save on well development costs, where applicable.

Produced water (PW) is defined here as all waters generated from O&G production post-drilling. PW accounts for the vast majority of the volume of fluids generated from oil and gas wells (Clark and Veil, 2015, 2009). Depending on the age and location of the well, the PW-to-oil volume ratio (WoR) can range from 3:1 to greater than 10:1 (Clark and Veil, 2009), with the ratio typically in the lower range (3:1 to 4:1) for shale reservoirs (Scanlon et al., 2014). Total U.S. PW volumes from both conventional and hydraulically fractured wells (referred hereafter respectively as “C-PW” and “U-PW”) are estimated upwards of  $880 \times 10^9$  gal ( $3.3 \times 10^9$  m<sup>3</sup>) annually (concomitant to the production of nearly  $95 \times 10^9$  gal ( $3.6 \times 10^8$  m<sup>3</sup>) of oil and  $30 \times 10^9$  ft<sup>3</sup> ( $8.5 \times 10^8$  m<sup>3</sup>) of natural gas), of which U-PW accounts for roughly  $150 \times 10^9$  gal ( $5.7 \times 10^8$  m<sup>3</sup>) per year (Clark and Veil, 2015; Silva et al., 2017; Thiel et al., 2015). U-PW currently accounts for a smaller portion (~17%) of the total U.S. PW volumes, but is expected to grow rapidly.

Reusing C-PW for O&G production is current industry practice (*e.g.*, water flooding), but HF wells present drastically different issues due to their innate lack of a “built-in” reservoir for water reinjection. U-PW is mostly disposed (~90%) by reinjection into more permeable rock; minimizing this volume would relieve concerns over induced seismic activity (Drummond and Grubert, 2017; Ellsworth, 2013; Jackson et al., 2014; Walsh and Zoback, 2015) and surface spills (McLaughlin et al., 2016; Shrestha et al., 2017). The repurposing of U-PW lowers the potential environmental impacts

of HF and raises the possibility of turning a waste into a valuable resource. In addition, the prospect of reusing and recycling U-PW could help minimize the O&G industry’s freshwater withdrawals, which – while relatively minor on a national scale (Dieter et al., 2018) – could impact local municipal and/or agricultural operations in arid and semi-arid regions (Echchelh et al., 2018; Nicot and Scanlon, 2012).

The need for an economical and environmentally sustainable approach for managing the U-PW is critical, given the enormous volumes that are expected to be generated in the coming years. Since 2000, total U.S. O&G production volumes have grown by nearly 55% and 45%, respectively. UGTO is currently the primary hydrocarbon feedstock in the U.S., and production volumes are projected to increase for at least the next two decades (U.S. Energy Information Administration, 2018). On this basis, projected PW volumes are expected to increase by  $50 \times$  and  $20 \times$  in unconventional gas- and oil-producing regions by 2030 (Kondash et al., 2018). In the next sections, we (1) provide an overview of the technical challenges and environmental concerns associated with treating U-PW, (2) suggest “fit-for-purpose” treatment options and best practices for industry, and (3) identify research needs and opportunities for new water treatment and reuse technologies.

## 2. Overview of the produced water problem

### 2.1. Hydraulic fracturing in the U.S

UGTO reservoirs have very low permeability (<0.1–10 μDarcy) (Bennion et al., 2000; Moghadam and Chalaturnyk, 2015; Scanlon et al., 2014) compared to conventional O&G reservoirs (~1–1000 mD). Thus, hydrocarbon recovery is more challenging in these tighter formations (Gerritsen and Durlafsky, 2005; Kazemi et al., 1976). This fluid is composed of water and proppant (typically sand or ceramic) at ~87 and 13 vol%, respectively (U.S. EPA, 2016a, 2015). Chemical additives account for <0.20 vol%, and can include friction reducing polymers (White and Mungal, 2008), cross-linked or liner gels (Barati and Liang, 2014; Stringfellow et al., 2014), biocides (Kahrilas et al., 2015), surfactants (Lester et al., 2015; Xu et al., 2012), and inhibitors for scale and corrosion (Lester et al., 2015; Stringfellow et al., 2014). The proppant is deposited and embeds into the new fissures, forming porous channels through which hydrocarbons and water then diffuse and flow up the well-bore to surface facilities for phase separation and recovery (U.S.

EPA, 2016a).

The use of HF technology in the U.S. dates back to the late 1940's, but it was not until ca. 2000 when this method was coupled with advanced directional drilling techniques (*i.e.*, horizontal/deviated wells) that recovering the nation's shale hydrocarbon resources became economically viable (Montgomery and Smith, 2010; Teff, 2018; U.S. EPA, 2016a). Nearly one-third of all US HF wells were constructed between 2000 and 2013, and from 2011 to 2014 an estimated 25,000–30,000 new wells were cracked annually (U.S. EPA, 2016a). Contributing <1% in 2000, HF operations accounted for >50% and >80% of U.S. oil and gas volumes, respectively, in 2017 (U.S. Energy Information Administration, 2018; U.S. EPA, 2016a).

## 2.2. Hydraulic fracturing internationally

This critical review focuses on onshore U.S. operations, with an emphasis on shale development (*i.e.*, UGTO). While interest in shale resources has spurred exploratory drilling internationally, U.S. production volumes are nearly  $100 \times$  that of the nearest producers, Canada and China (International Energy Agency, 2017). Explorations in the United Kingdom (Cotton et al., 2014) and continental Europe have yet to yield commercial shale-gas wells, as of 2016 (De Silva et al., 2016; Inman, 2016). Similarly, Australian ( $396 \times 10^{12}$  ft<sup>3</sup> (396 Tcf or  $11.2 \times 10^{12}$  m<sup>3</sup>) of recoverable shale gas) and South American development is an ongoing technical, political, and economic debate, although Argentina's Vaca Muerta play (308 Tcf ( $8.7 \times 10^{12}$  m<sup>3</sup>) of technically recoverable shale gas and  $16 \times 10^9$  barrels (Bbbls or  $1.9 \times 10^9$  m<sup>3</sup> of oil) is particularly promising (De Silva et al., 2016; Gomes and Brandt, 2016; Mauter et al., 2014; U.S. Energy Information Administration, 2013).

China, despite containing the world's largest shale reserves at ~1115 Tcf ( $31.6 \times 10^{12}$  m<sup>3</sup>) of technically recoverable shale gas and 32.2 Bbbl ( $3.84 \times 10^{12}$  m<sup>3</sup>) of tight oil has yet to achieve full-scale commercial development (Kuuskraa et al., 2013) due in part to logistical and geological complexity. Water used for fracturing operations in areas such as the Fuling gas field is expected to exceed 50% of the water used in U.S. operations (total of  $10.5 \times 10^9$ – $32.7 \times 10^9$  gal or  $39.9 \times 10^6$ – $123.9 \times 10^6$  m<sup>3</sup>). Median values of water required on a per-well basis in the Sichuan Basin ( $9 \times 10^6$  gal/well or  $3.4 \times 10^4$  m<sup>3</sup>/well) and Fuling field ( $8 \times 10^6$  gal/well or  $3.0 \times 10^4$  m<sup>3</sup>/well) of Chongqing Province are also greater than in most of the U.S. ( $2.6 \times 10^6$ – $5.3 \times 10^6$  gal/well or  $9.8 \times 10^3$ – $2.0 \times 10^4$  m<sup>3</sup>/well) (Guo et al., 2016; Zou et al., 2018).

Canada has promising shale deposits with technically recoverable shale gas and oil of 573 Tcf ( $1.62 \times 10^{13}$  m<sup>3</sup>) and 8.8 Bbbl ( $1.05 \times 10^9$  m<sup>3</sup>), respectively under development in British Columbia (Montney, Horn River and Liard basins), Alberta (DuVernay, Muskwa, Basal Banff, Montney, and the Colorado) and Saskatchewan (Bakken - Williston basin) with the technical practices closely mirroring those in the U.S. (Alberta Energy Regulator, 2015). In addition, environmental regulations in Canada, as in the U.S., are a combination of subnational (*e.g.*, province, state) and national policies (Carter and Eaton, 2016). In 2017, total water volumes used for HF in Alberta were over  $6.34 \times 10^9$  gal ( $24 \times 10^6$  m<sup>3</sup>) including non-saline water and 4% recycled water combined; while British Columbia reportedly used  $2.3 \times 10^9$  gal ( $8.8 \times 10^6$  m<sup>3</sup>) (Alberta Energy Regulator, 2018). To keep with the technical (rather than regulatory) focus of this work, we do not discuss further PW in Canadian UGTO basins.

We also omit water treatment discussions for offshore operations, as they have been discussed elsewhere (Clark and Veil, 2015; Fakhru'l-Razi et al., 2009; Zheng et al., 2016). Only 3% of the total U.S. PW volumes in 2012 came from offshore operations, and its management differs greatly due to infrastructure restrictions (Clark and Veil, 2015).

## 2.3. The hydraulic fracturing water cycle

While this article focuses on end-use implementation, an understanding of the other stages is necessary to address treatment goals. The HF water cycle consists of five stages: acquisition, fluid mixing, injection, U-PW handling, and end-use implementation (U.S. EPA, 2016a). Fluid mixing describes the process of formulating fracturing fluids. No standard formula exists; formulation is a function of the well geology and depth, initial water quality, and operator discretion. In general, these mixtures are >99.8 wt% water and proppant mixed with <0.2 vol% of additional chemicals (U.S. EPA, 2016a, 2015). Chemical disclosure registries, such as the Ground Water Protection Council and Interstate Oil and Gas Compact Commission's *FracFocus*®, document additives on an individual well basis (GWPC and Interstate Oil and Gas Compact Commission IOGCC, 2014).

Freshwater is by far the largest volume component used in the development of these fracturing fluids. As an example, from 2000 to 2011, the cumulative freshwater usage for shale gas HF operations was reported to vary throughout Texas from  $1.7 \times 10^9$  gal ( $6.5 \times 10^6$  m<sup>3</sup>, Haynesville), to  $4.8 \times 10^9$  gal ( $18 \times 10^6$  m<sup>3</sup>, Eagle Ford), and up to  $38.3 \times 10^9$  gal ( $145 \times 10^6$  m<sup>3</sup>, Barnett) (Nicot and Scanlon, 2012). To place this in context, water used across the entire Barnett development in 2010 was ~9% of the  $81.4 \times 10^9$  gal ( $308 \times 10^6$  m<sup>3</sup>) consumed by the nearby city of Dallas (2010 population of 1.2 million) that same year, and significantly less than the annual average statewide consumption of  $5.22 \times 10^{12}$  gal ( $19.8 \times 10^9$  m<sup>3</sup>, including rural communities) (Nicot and Scanlon, 2012; TWDB, 2015). Similarly, in North Dakota the total freshwater used for HF activities in the Bakken from 2005 to 2013 was  $15.8 \times 10^9$  gal ( $59.9 \times 10^6$  m<sup>3</sup>) (Scanlon et al., 2014). From 2005 to 2014, the cumulative HF water volumes for 10 of the largest U.S. formations (*e.g.*, Barnett, Bakken, Eagle Ford, Marcellus, Niobrara, Permian and others) was roughly  $250 \times 10^9$  gal ( $940 \times 10^6$  m<sup>3</sup>) (Kondash and Vengosh, 2015; Scanlon et al., 2014).

Initial water acquisition, and the subsequent U-PW handling, are dictated by the remote locations of well sites. In some cases, no centralized infrastructure exists, so the initial assessment and site construction can take on the order of 10–16 weeks (U.S. EPA, 2016a). In preparation for U-PW, a variety of options are implemented depending on the region-specific regulations, site logistics, and/or projected water volumes (Groundwater Protection Council, 2009; U.S. EPA, 2016a). Above-ground storage tanks (ASTs) are typically closed-loop systems in which PW is directly transferred from the wellhead through interconnecting pipelines (U.S. EPA, 2016a). These tanks can be either open or closed to the environment and provide intermediate storage before the PW is either trucked off-site or, in some cases, reused at the well. Less often, lined earthen pits are built as open-air holding ponds. While regulations have gradually phased-out this method on a national scale, pits are still common practice in specific, high-producing regions of the country such as Texas (Railroad Commission of Texas, 2018) (Barnett and Permian Shale) and in some rare instances in the Green River Basin (Lyman et al., 2018). Finally, it should be noted that U-PW generated during the first few weeks of production is often referred to as "flowback water" to differentiate from water associated with long-term, post-flowback production (Rosenblum et al., 2017). This distinction is made because flowback water can contain larger quantities of residual HF chemicals, sand, silt, and proppant from the near-wellbore after initial well production begins, presenting a very different water profile than post-flowback, or produced, water. This temporal variability can have a significant influence on the viability of management options during the first ~21 days of production, highlighting that suitable treatment technologies should exhibit flexible capacities even at a single well site (Oetjen et al., 2018).

## 2.4. Produced Water Characteristics

The chemical and ion content of U-PW (as well as C-PW) are highly variable and dependent on well location, geology, and operational parameters. U-PW composition variability arises primarily from “formation waters” found naturally alongside entrapped hydrocarbons. Water salinity and total dissolved solids (TDS) correlate with the geological basin (shale play) and well depth (Khan et al., 2016; Shaffer et al., 2013). For example, amongst the “big four” U.S. plays (i.e., Bakken, Eagle Ford, Permian, and Marcellus) (U.S. Energy Information Administration, 2015), the Bakken region around North Dakota has TDS exceeding 200,000 mg L<sup>-1</sup>, whereas Pennsylvania’s Marcellus shale averages closer to 100,000 mg L<sup>-1</sup> (Maguire-Boyle and Barron, 2014; Shaffer et al., 2013; U.S. EPA, 2016a). More recent work has also showcased the strong geographic dependence of dissolved organic carbon and bacterial speciation (Wang et al., 2019). Note that the level of trace hydrocarbons in U-PW storage facilities is highly dependent on the efficacy of local separation equipment (e.g., free-water knockout) and operator competency.

In general, the TDS in U-PW ranges from brackish (10,000 mg L<sup>-1</sup>) to nearly saturated (>260,000 mg L<sup>-1</sup>) with chloride, sulfide, sulfate, carbonate, and alkali and/or alkaline earth metals being the dominant ions. In extreme cases, the TDS can approach 400,000 mg L<sup>-1</sup>, >10 × saltier than seawater (~35,000 mg L<sup>-1</sup>), at which point solids precipitation is inevitable due to supersaturation (Shaffer et al., 2013; U.S. EPA, 2016a). Naturally occurring radioactive materials (NORMs) are another challenge in U-PW and are present predominantly as radium-226 and radium-228 sulfates that have co-precipitated with barium and strontium sulfate scales (Chapman et al., 2012; International Association of Oil and Gas, 2008; Rowan et al., 2011). Total organic carbon (TOC) originates from fracking fluid additives, treatment chemicals, and trace oil and grease, with typical concentrations <1000 mg L<sup>-1</sup> but can approach as high as 6000 mg L<sup>-1</sup> (Maguire-Boyle and Barron, 2014). Total suspended solids (TSS) including silica, metal oxides, and other minerals are also commonly encountered.

Bacterial invasion and proliferation can be severely problematic for HF operations. Down-well formation of biofilms over the fractured pores, proppant pack, or other flow paths can impede hydrocarbon extraction. Sulfate-, thiosulfate-, and sulfur-reducing bacteria (SRB) present an environmental/health hazard from the bio-production of hydrogen sulfide (H<sub>2</sub>S) and an operational threat due to the potential for well souring, which can often represent a substantial cost for operators (Gaspar et al., 2014; Gieg et al., 2011). Moreover, acid producing bacteria (APB) and SRB both threaten wellbore tubulars and pipelines due to microbially influenced/induced corrosion (MIC) (Enning and Garrelfs, 2014). Corrosion products (e.g., organic acids) and common precipitates (such as iron oxides and iron sulfides) can damage drilling equipment, threaten wellbore integrity, and ultimately shorten the lifespan of the well (Alley et al., 2011).

We identify ten contamination metrics to assess U-PW quality: Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Scale, Hardness, Iron, Sulfate, NORMs, Heavy Metals (RCRA8), Organics, and Bacteria. Fig. 1 highlights the major shale plays across the U.S. that have been considered in this study and illustrates the vast variation of their concentrations across the U.S. for wells drilled since 2000. Further data may be found in the SI (Table S1.) All data are sourced from the U.S. Geological Survey National Produced Waters Geochemical Database v2.3 (Blondes et al., 2018). Scale is defined here as the combined barium (Ba), strontium (Sr), calcium (Ca), magnesium (Mg), and iron (Fe) ion concentrations that have precipitated with sulfate, carbonate or sulfide anions, whereas

Hardness is defined exclusively as the combined Ca<sup>2+</sup> + Mg<sup>2+</sup> concentration in solution. This distinction has been made to facilitate comparisons across various water treatment industries (e.g., municipal waste treatment) where these terms are sometimes, at least colloquially, used interchangeably.

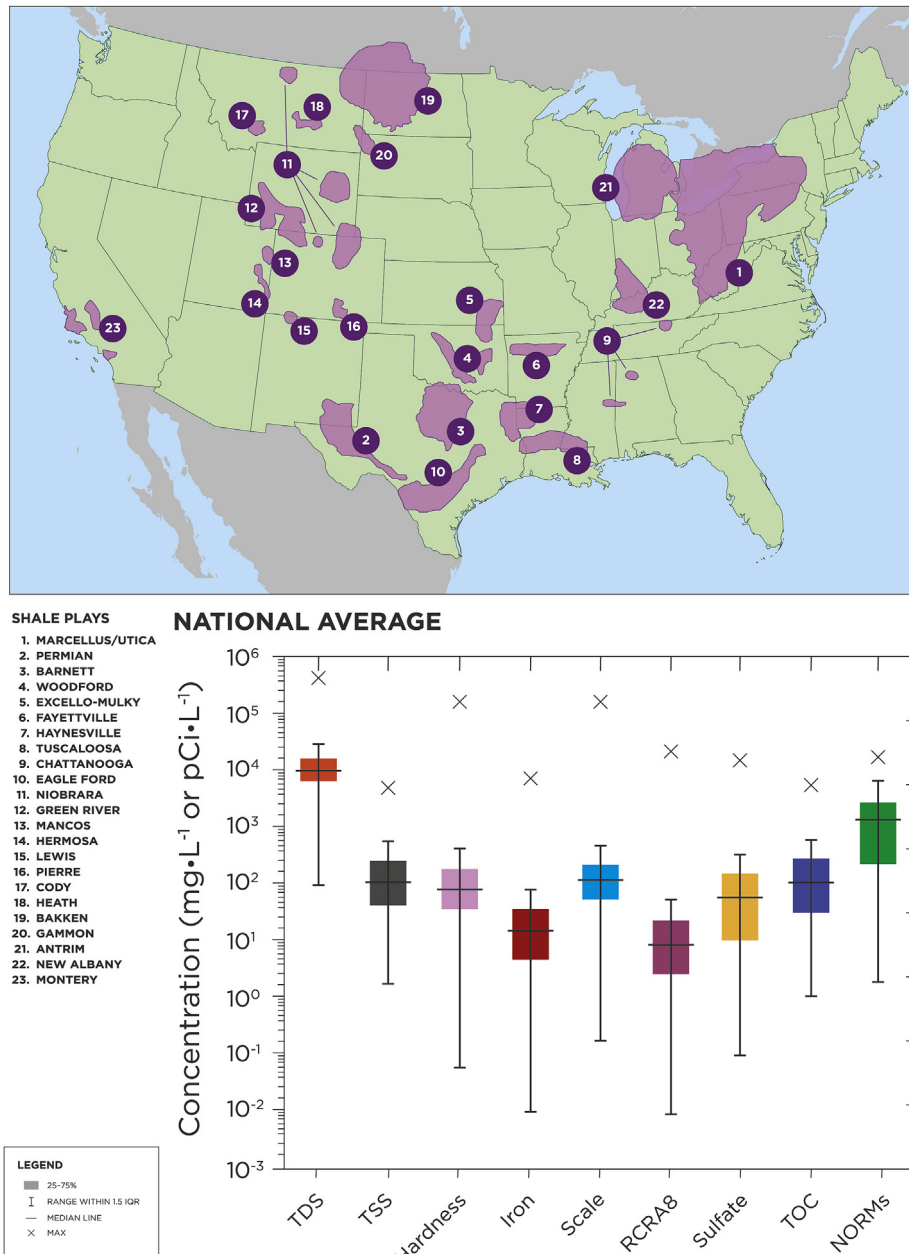
Iron describes dissolved and precipitated Fe(II)+Fe(III) species. Sulfate is the cumulative concentration of all sulfate species (e.g., FeSO<sub>4</sub>, BaSO<sub>4</sub>, etc.). NORMs represent the total concentration of Ra-226 and Ra-228. Several other radioactive elements (e.g., Rn-222, Sr isotopes) have been documented in PW; however, national reporting of these elements is sparse whereas Ra-226 and Ra-228 are commonly measured. The concentration of heavy metals has been defined as the cumulative concentration of arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se), and silver (Ag), as defined by the U.S. Resource Recovery and Conservation Act (i.e., RCRA 8) (U.S. EPA, 2017). The value of Organics is taken as the Total Organic Carbon (TOC) content of the water. The working definition of Bacteria used here is simply the total bacterial counts per volume of water (count · 100 mL<sup>-1</sup>) – no distinction is made between species or function (e.g., SRB, APB). However, reporting a “national average” for bacterial concentrations would be misleading. Bacterial control is already a central concern for oil-field operators (Kahrilas et al., 2015), and this extends to the mitigation of bacterial growth in the PW ponds/storage tanks. A similar analysis for the eight largest producing shale plays (as opposed to the national average illustrated in Fig. 1) may be found in Fig. S1.

Elemental analyses, organic classifications, bacterial speciation, and NORM measurements, for specific wells across the U.S. are not discussed here (Akob et al., 2015; Barbot et al., 2013; Harkness et al., 2015; Lutz et al., 2013; Oetjen et al., 2018; Orem et al., 2007; Thacker et al., 2015). Overall, U-PW is a highly variable and chemically complex water matrix that poses site-specific treatment and reuse challenges. We conclude that treatment technologies must be tailored to the localized water quality and specific needs of the intended end-use. Compounded with region-specific regulations, well site logistics, economics, and differing field development goals, a “one-size-fits-all” treatment methodology is unfeasible.

## 3. Current PW management practices

### 3.1. Overview of potential options

Here, we identify three general end-use categories: *Disposal*, *Reuse*, and *Recycle*. *Disposal* describes end-uses with no subsequent purpose or utility, such as direct injection into a disposal well, evaporation, or surface discharge. Treatment towards disposal prioritizes solids, oil, and microbial contaminant mitigation as well as regulatory compliance. *Reuse* goals are those focused towards *internal reuse* to further hydrocarbon production, such as HF or enhanced recovery. Reuse could potentially close the water cycle for drilling and fracturing operations, thus alleviating strains on freshwater withdrawals (Entrekin et al., 2018), minimizing water transportation activities (Lutz et al., 2013), and mitigating environmental contamination risks (Lauer et al., 2016; McLaughlin et al., 2016). Internal reuse treatment is broadly defined but usually focuses on reducing solids, residual oil & grease, iron and certain chemical additives from HF that could interact with the specific planned reuse option while leaving the TDS unchanged. *Recycle*, or “beneficial disposition,” describes implementing PW for an alternative purpose (Echchel et al., 2018). Requirements for this category can differ greatly, but will usually require desalination. For example, the required water quality for crop irrigation (Ayers and Westcot, 1985; Olkowski, 2009; U.S. EPA, 2012b) is far more stringently regulated than waters used for road dust/ice control



**Fig. 1.** (Top) Map of contiguous U.S. outlining the 24 shale deposits considered in this study. (Bottom) Box and whisker plot of the national averages (logarithmic scale) for nine of the ten identified contamination metrics for 12,711 individual wells. Note that an average bacterial concentration is not reported. Tabulated data are presented in Table S1. Shale-specific data for the eight highest producing plays are presented in Fig. S1.

(Goodman, 2017; North Dakota Department of Health). To emphasize this point, a few recycle examples have been selected ranging from those that are currently in-use to those that are simply proposed ideas (e.g., potable water (Sabie and Fernand, 2016)). This discussion should not be considered a comprehensive list. For additional context, regulatory requirements for water disposal on a state-by-state basis may be found using the *FracFocus* search engine (GWPC and Interstate Oil and Gas Compact Commission IOGCC, 2014).

Precise figures for PW volumes on a national scale are not readily available. Surprisingly, although recovered O&G volumes have been rigorously documented since industrial production first began, monitoring of PW volumes has only been performed in the last few decades; and U-PW specifically was not monitored as its own category until 2008 (in the Barnett Shale) (Clark and Veil,

2009; Lewis and Hughes, 2008) and is in fact still not separately identified in some regions. Moreover, while it is becoming commonplace to report PW volumes, documenting its subsequent management remains rare. To the best of our knowledge, the most recent report of this nature was based on data gathered in 2012 (Clark and Veil, 2015). More recent reports on the “Big Four” U.S. Shale regions suggests that, from 2011 to 2016, U-PW volumes generated within the first production year increased by up to 1440% in some regions, reflecting an increase in per-well water use of up to 770% (Kondash et al., 2018) – emphasizing the dynamic, evolving nature of this issue. However, despite the evident annual variations in the precise water volumes utilized in UGTO operations, we estimate that the dominant PW management practices have remained comparatively consistent on a national scale.

### 3.2. Current Practices

The lack of complete, high-quality data limited our ability to quantify the water balance for UGTO production separately from the water balance for the overall O&G production. In 2012 over 90% of all PW (from conventional and UGTO wells) was estimated to have been reinjected underground, of which ~40% was injected into onsite disposal wells, ~45% was transported and injected into offsite disposal wells, and ~45% was used for enhanced recovery (Fig. 2) (Clark and Veil, 2015; Veil and Clark, 2011). Besides re-injection, roughly 4% of PW was evaporated, 3% was discharged to the surface (note that this particular practice is becoming increasingly prohibited in light of evolving regulations), and the rest was either sent to third-party businesses for treatment or reused in fluid formulations (Clark and Veil, 2015).

For U-PW specifically, we estimate that a far greater majority (>90%, national scale) of the water reinjected underground is targeted towards disposal wells (onsite or offsite) given that PW cannot be implemented for enhanced recovery in unconventional wells. That is, most U-PW is currently disposed, highlighting the opportunity to increase its reuse. Again, although reliable national statistics are lacking, this point has been showcased clearly in recent sub-national investigations such as the Bakken (Shrestha et al., 2017) in which >95% of U-PW was disposed. Note that a key exception to this national trend is the Marcellus region (Hill et al., 2019) where recent regional regulations have led to a significantly greater amount (~50%) of U-PW to be reused within the state to fracture new wells, which is reflected by a decrease in the average distance traveled by surfaced water to a end-use location from 95 miles in 2012 to 23 miles in 2017. However, even in Pennsylvania, a state that has arguably the most rigorous documentation of PW management practices, nearly one-third of all liquid waste generated from 1991 to 2017 does not have a reported final destination (Hill et al., 2019).

Disposal injection requires high permeability formations that can be saturated with PW, effectively acting as subsurface storage. This is commonplace in, for example, the Delaware and Midland Basins of Texas and is considered safe practice by regulatory agencies (Vidic et al., 2013). However, injection has been scrutinized for its association with elevated seismic activity (Davies et al., 2013; Drummond and Grubert, 2017; Ellsworth, 2013; Jackson et al., 2014), groundwater contamination (He et al., 2017; Luek and Gonsior, 2017), and

possibly even surface water contamination (Akob et al., 2016; Kassotis et al., 2016) in select areas. Disposal injection treatment prioritizes lowering the TSS such that well and/or formation pores are not plugged and equipment/well integrity is not compromised (Jiménez et al., 2018). The relative ease and low cost of this practice provides its appeal, but onsite disposal-well availability can be limited (*i.e.*, in areas with intensive drilling or restrictive regulations), requiring then PW to be transported by trucks offsite.

Reusing PW by reinjecting it into a producing formation (*i.e.*, water or steam flooding) is a widely practiced enhanced recovery method for conventional wells (Clark and Veil, 2015). As a well ages, the output rate decreases due to diminished down-well pressures. Water flooding involves pumping the fluid into the reservoir to offset the lost extraction volume, increase pressure, and stimulate transport of the remaining hydrocarbons. This logical end-use for C-PW does not apply for U-PW, as the low-porosity shale and carbonate formations have minimal pore volume that may be saturated with water.

### 3.3. Current treatment technologies

Current PW treatment approaches, and some promising treatment technologies, have been the subject of several excellent reviews (Colorado School of Mines, 2009; Fakhru'l-Razi et al., 2009; Jiménez et al., 2018; Silva et al., 2017). The following section provides an overview of a typical PW treatment train currently used in industry (Fig. 3), with the objective of highlighting (in Section 4) how emerging technologies may be used to bridge the gap in treatment capabilities within a fit-for-purpose framework. Physical methods (*e.g.*, filtration, adsorption) are applicable to inorganic and organic contaminants but can be impractical and cost prohibitive for particularly high TDS and/or TSS waters due to excessive fouling, plugging, scaling, and/or large quantities of sludge generation. Chemical methods, particularly chemical oxidation, are common for bacterial control and/or to decompose refractory organics. Sequential chemical-physical methods entail adding an active chemical species, such as a flocculant or complexing agent, and then physically removing the ensuing product. This approach is well established in municipal water treatment (Lee et al., 2014), but still exhibits the aforementioned shortcomings of purely physical processes. Large, expensive infrastructure (*e.g.*, clarifier or settling tanks) is required for these approaches to be practical.

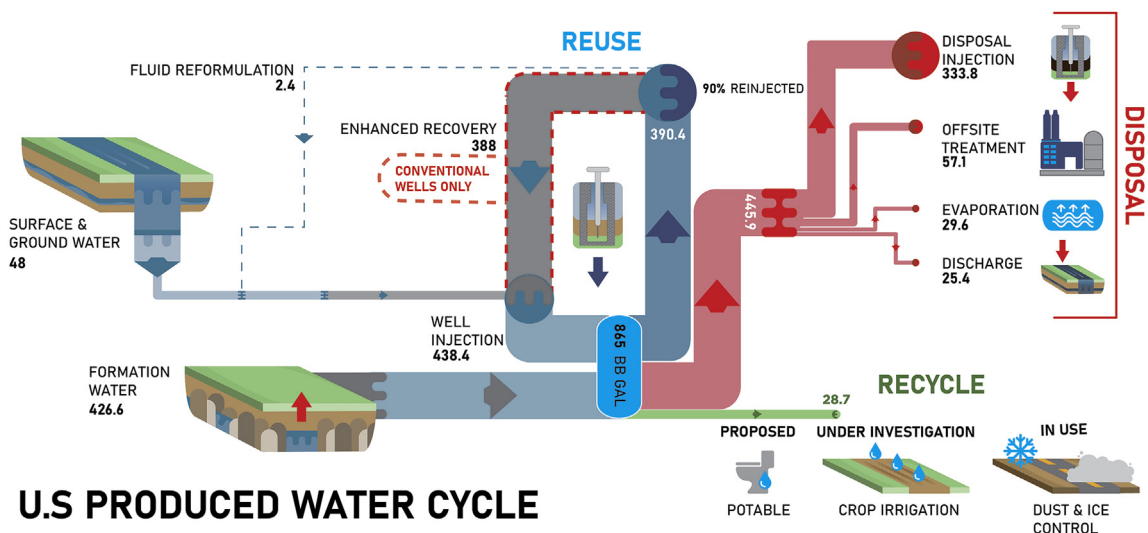
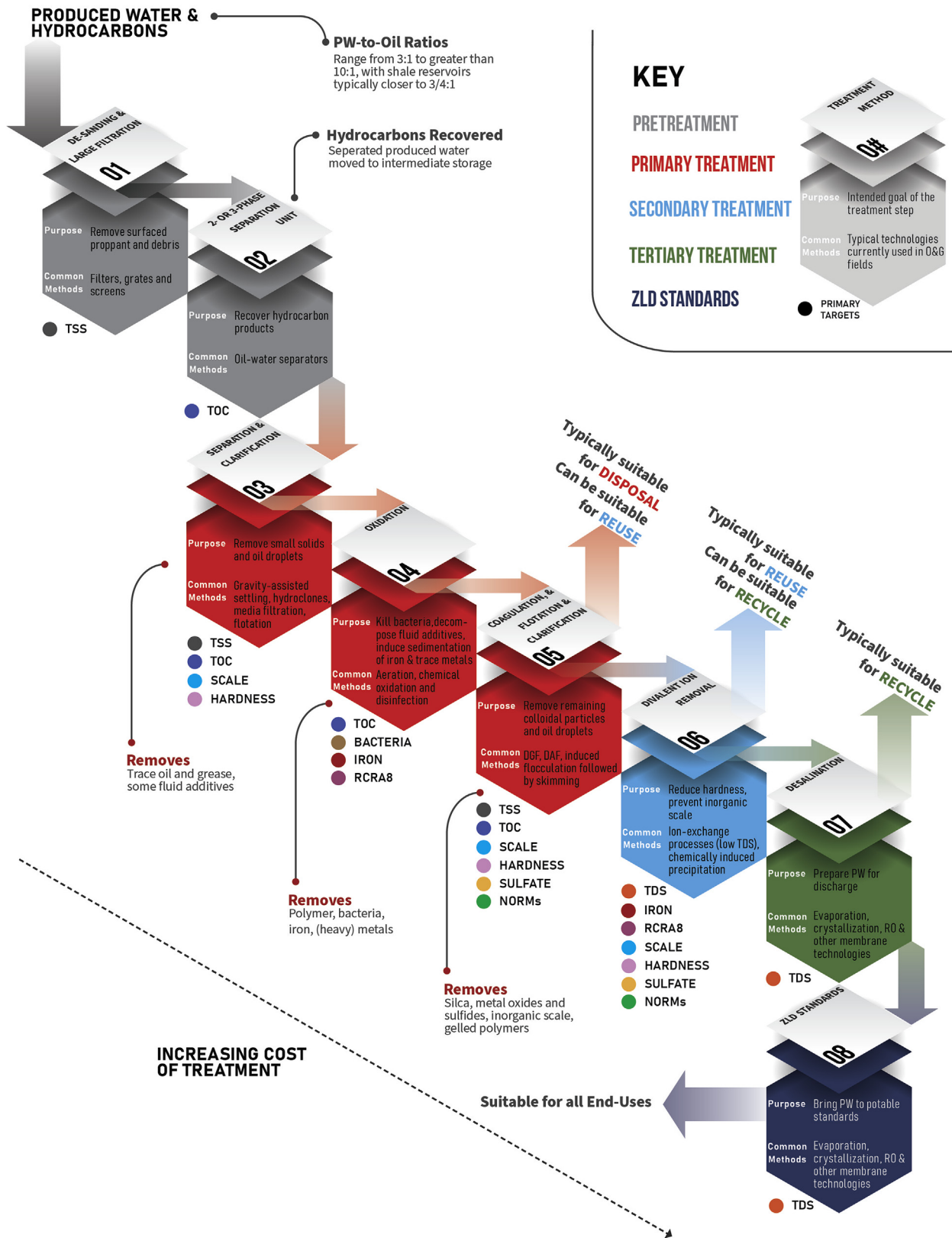


Fig. 2. Produced water cycle (for combined unconventional and conventional sources) for onshore U.S. operations based on 2012 values. Recycle end-uses (*e.g.*, crop irrigation) are common examples. Water volumes are estimated (with units of billions of gallons per year) (Clark and Veil, 2015; Kondash and Vengosh, 2015; U.S. EPA, 2016a).



**Fig. 3.** Block flow diagram of current produced water treatment methods (unconventional and conventional sources). The primary target contaminants, and primary technologies used to accomplish each are provided. Boxes are color-coded to indicate pretreatment (gray), primary treatment (red) secondary treatment (blue), tertiary treatment (green), and treatment towards zero liquid discharge (ZLD) standards (navy). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Current technologies for U-PW treatment are frequently categorized into primary, secondary, and occasionally tertiary treatments based primarily on the TDS/salinity of the water (Arthur et al., 2005). A fourth treatment level, zero-liquid discharge (ZLD), is considered when treat-to-release of U-PW is permitted by regulatory agencies. Primary treatment methods target removal of most solids, residual oil & grease, iron, fracturing fluid additives and bacteria. Secondary treatment entails removal of multivalent ions including  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  that escaped primary treatment measures. These ions can adversely affect the performance of fracturing fluid additives during internal reuse and contribute to scaling tendencies when mixed with incompatible waters. Tertiary treatment processes enable full salt removal through desalination and specialized filtration technologies.

In a typical UGTO operation, the produced oil, gas, and water are first separated at the wellhead using 2- or 3-phase separation equipment to prepare the hydrocarbons for sale (American Petroleum Institute, 1990). De-sanding and/or simple filtration systems such as sock filters are often implemented prior to these separators to remove proppant and other large debris. The aqueous phase effluent is then further treated at a saltwater disposal (SWD) facility or central processing facility (CPF) prior to disposal by well injection, modification for internal reuse, or occasionally permitted release utilizing an assortment of treatment technologies discussed in the following sections. The block-flow diagram provided in Fig. 3 illustrates the typical treatment train associated with current produced water management practices.

### 3.3.1. Separation and Clarification

Separation and clarification technologies are selected based on water quality and facility economics with the goal of removing the smallest solids and oil droplets that passed through the oil-water separators. Present solid particles can include silica, metal oxides and sulfides, inorganic scale and gelled polymers. Settling ponds, frac pits, and above-ground storage tanks (ASTs) utilize quiescent, gravity-assisted phase separation to provide low cost removal of the densest solids with moderate retention times (12–48 h). The primary drawbacks to settling ponds/pits include a need for animal deterrent systems, multiple liners to prevent containment loss, leak detection capabilities, and often a large physical footprint (4–21 million-gallon capacity). Dynamic methods of separation include hydroclones, media filtration, and floatation equipment that can remove solids in a continuous manner at shorter residence times.

Media filtration uses silica sand, alumina, carbon beds, glass beads and walnut shells (Rawlins and Sadeghi, 2018). Walnut shells, in particular, are rapidly growing in popularity as they are an inexpensive, renewable filtering agent that can typically be disposed of in landfills. Defining characteristics of these technologies are that they provide very high (near complete) water recovery, require zero to minimal additional infrastructure, and are universally applicable to PW (*i.e.*, these technologies are not limited by TDS or inorganic ion content/speciation). In practice, approaches under this category may be easily scaled to accommodate any oil and grease concentrations typically encountered in the field, but inherently generate an additional solid waste (sludge) stream that must be disposed.

### 3.3.2. Oxidation

After simple filtration, a common first option for U-PW primary treatment is to send the aqueous phase to an oxidation unit that decomposes fracturing fluid polymers and additives, kills bacteria, and induces sedimentation of dissolved iron or other trace metals as metal oxides. Commonly used chemical oxidants for U-PW include sodium hypochlorite, chlorine dioxide (Erkenbrecher et al.,

2015), ozone, organic peracids (De Paula et al., 2013), hydrogen peroxide and oxygen *via* addition through aeration. Less common options include chlorine gas and permanganate, but the inherently greater safety hazard associated with the storage and handling of these oxidants in remote locations limits their practicality. Similarly, chlorine dioxide requires additional care due to its low boiling point (11 °C) and instability toward decomposition. Fracturing fluid chemicals can decompose into a plethora of products in either the wellbore, due to elevated temperatures, or in the well and/or oxidation unit due to oxidative damage (Weaver et al., 2003; Xiong et al., 2018). It should be noted that degradation products from oxidation unit effluents have not yet been fully quantified, presenting an opportunity for future research. As with *Separation and Clarification* processes, (chemical) oxidation is not typically restricted by water TDS or ion content and provides the appealing benefit of complete water recovery.

Several of the contaminants in U-PW (*e.g.*, iron, sulfate, nitrates, organics, polymers) can provide a source of nutrition for microbes. SRBs and APBs are the main microbial invaders in U-PW and can be treated using either chemical oxidants or non-oxidizing biocides (Kahrilas et al., 2015). For operators, chemical oxygen demand (COD) and chloride residuals are standard measurements to qualify biocide effectiveness and bacterial counts before and after treatment and are typically reported using standard NACE protocols which include techniques such as serial dilution bottle tests, radio-respirometry, and ATP photometry (NACE, 1994). More recently, emerging Advanced Oxidation Process (AOP) technologies such as electrochemical and electrocatalytic oxidation are undergoing development in the water treatment industry to replace bulk chemical oxidants and to further improve safety, reduce field inventory, and optimize manpower. While a detailed discussion of AOP technologies is provided in a later section, it must be noted now that a small number of oil-field service entities currently offer commercialized variants of these technologies. For example, the electrolysis of high chloride PW with 58–120 ppm ammonia was shown to generate chloramine *in-situ* which subsequently functioned as an effective biocide; achieving a 10-log reduction in SRB and APB counts during pilot tests in the Fayetteville shale (Boal and Mowery, 2015).

### 3.3.3. Coagulation, and floatation and clarification

Colloidal particles and oil droplets are usually too small to remove from water during the early separation and oxidation treatments, yet these contaminants must be removed prior to even subsurface disposal of U-PW to avoid well impairment. To achieve this, inorganic salts of ferric iron or aluminum sulfate (alum) are mixed into the U-PW with agitation to destabilize emulsions, disrupt charged particles and coagulate polymers/surfactants in a process called coagulation-flocculation. The ferric and alum salts form 3-D networks that help trap fine contaminants in their matrix resulting in a more clarified U-PW (Gebbie, 2006). These materials then coagulate and float to the top of the treatment tank for removal by skimming. Some operators, especially in conventional O&G facilities, use dissolved gas floatation (DGF) or dissolved air floatation (DAF) equipment to remove the coagulated sediment in a continuous manner (Sport, 1969). DAF and DGF accomplish this by injecting gas or air bubbles into the tank to 'float' the agglomerated solids to the surface where they are removed by a mechanical skimmer. The clarified aqueous phase is removed from the bottom of the tank and sent to the next processing step. Challenges to using this equipment include complications that arise due to the adhesive nature of the flocculant leading to undesirable coating and tank fouling during skimming operations. As with the other aforementioned primary treatment options, the appeal of these methods is that they are not typically restricted by the severity of the TDS or



inorganic ion concentration. Note that while these methods inherently require an investment in additional infrastructure, they benefit from decades of refinement and optimization in conventional O&G PW treatment.

Finally, divalent metals, including  $\text{Ca}^{2+}$  and  $\text{Fe}^{2+}$ , are precipitated chemically using alkali (carbonate, hydroxide or sulfate) salts (see Section 3.3.4). Water in this condition, now void of most oil contaminants and solids, can be stored for reuse in fracking operations or disposed by well injection. A best-practice is to provide a biocide treatment to manage microbial growth using either commercial non-oxidizing biocides or chemical oxidants prior to injection into the disposal well.

### 3.3.4. Secondary treatment – divalent ion removal

Preventing inorganic scale, reducing water hardness, and removing problematic divalent ions (e.g., NORMs, iron) from U-PW are the goals of secondary treatment processes. Whereas primary treatment methods are characterized by their robust capabilities and near universal applicability, secondary treatment processes have more variable capabilities and are more restricted by PW quality and process economics. Most divalent ions present in PW are alkaline earth metals and iron although sulfate and carbonate are included in this description. Removing these ions is important to address concerns of potential NORM or inorganic scale forming in the disposal well due to mixing of incompatible waters. In HF operations where crosslinked guar polymers are used, the boron or metal-based crosslinking agents that viscosify these polymers can end up in U-PW and should be removed in this stage to avoid future chemical compatibility issues. Traditional methods for removing the divalent  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ra}^{2+}$  and  $\text{Mg}^{2+}$  are sparse, but include adding sulfate or carbonate ions to the water (i.e., lime softening) to induce precipitation of the metals as the metal sulfates or carbonates (Folio et al., 2018). An advantage to this approach is the operational simplicity, less-restrictive TDS constraints ( $\text{TDS} > 100,000 \text{ mg L}^{-1}$ ), and low cost.

For low salinity PW, ion-exchange processes are sometimes used to 'soften' the water by removing the hardness ions (Brown and Sheedy, 2002). It is important to have first removed most TSS (particularly oxidized metals) and oil and grease during primary treatment to avoid fouling of the exchange resins. Weak acid resins are effective for water where  $\text{TDS} > 3000 \text{ mg L}^{-1}$ ; yet require special metallurgy and significant pH adjustments in between uses to regenerate the resins. Strong acid cations are less effective for water treatment when  $\text{TDS} < 3000 \text{ mg L}^{-1}$  but are very durable and do not require significant attention to pH or complicated reactor design. In general, ion-exchange processes are applicable for TDS concentrations between 500 and 7000  $\text{mg L}^{-1}$  (Colorado School of Mines, 2009) As discussed in greater detail in Section 4, promising emerging technologies for this application (i.e., preferential removal of multivalent ions over monovalent) include nanofiltration ( $\text{TDS} \sim 500\text{--}25,000 \text{ mg L}^{-1}$ ) and electrically driven (charge) separation approaches (e.g., CDI). Currently, the suite of technologies which can be classified as dedicated secondary treatment methods is limited and presents an inviting opportunity for future research and case studies.

### 3.3.5. Tertiary treatment – desalination

Tertiary treatment methods target salt removal to reduce TDS and possibly iron or other (heavy) metals that passed through the primary and secondary treatments (i.e., desalination). The leading technology options in this treatment class include evaporation, distillation, crystallization, and (reverse, forward or hybrid) osmosis, albeit with limitations. For example, while reverse osmosis (RO) is remarkably efficient for removing dissolved solids, the maximum tolerated feed TDS is  $\sim 45,000 \text{ mg L}^{-1}$ . Thus, RO

would likely need to be the final treatment step after high salt removal depending on the initial PW quality. For high TDS PW ( $> 40,000 \text{ mg L}^{-1}$ ) distillation technologies (e.g., multi-stage flash, vapor compression, mechanical vapor compression) are viable options, but are prone to scaling when treating waters with elevated multivalent cation concentrations (underscoring the need for additional secondary treatment technologies) and suffer from low water recovery rates and high energy costs (Colorado School of Mines, 2009).

Most tertiary treatment options are constrained by the process economics, equipment, and footprint and are therefore seldom performed unless required by regulatory agencies. This level of treatment is typically only seen in regions of the country that strictly limit the use of disposal wells and discharge volumes (e.g., Marcellus) (Hill et al., 2019; Shaffer et al., 2013). It is worth mentioning that these regulatory restrictions have contributed to an economic environment in which relatively high energy, offsite treatment approaches (e.g., crystallizer technology) are viable options for U-PW management. As discussed in the following section, desalination technologies benefit from a comparatively greater amount of dedicated research effort in the academic community. Emerging approaches, ranging from a host of membrane-based technologies to electrically driven ion removal methods, all seek to minimize energy consumption and improve water recovery rates.

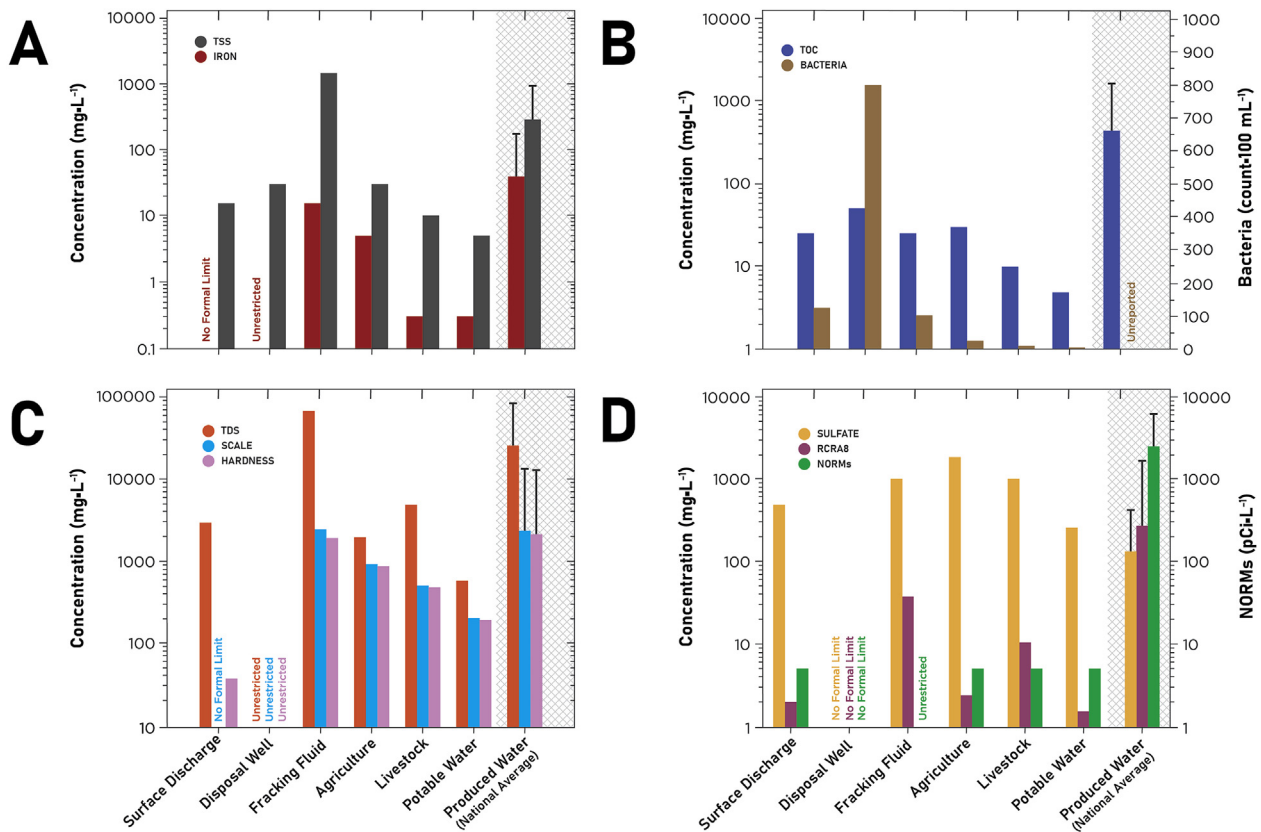
## 4. Emerging end-use opportunities and U-PW fit-for-purpose treatment options

### 4.1. End-use selection and research philosophy

The variation in U-PW quality and treatment objectives implies that technologies must adopt a "fit-for-purpose" philosophy to match the treated water quality to the intended use (Alvarez et al., 2018; Anastas and Zimmerman, 2007). Starting water quality dictates the feasibility of a treatment method and the potential end-uses. To emphasize this, Fig. 4 provides a comparison between the national average for each of the ten established contamination metrics in PW (defined under *Produced Water Characteristics*) and the required treatment objectives of six representative end-uses, which were selected to span promising options for reuse (e.g., fracking fluid), recycle (e.g., agriculture, livestock, potable), and disposal (e.g., well injection, surface discharge) goals. These six end-uses should not be considered an exhaustive list, but were chosen to illustrate that the desired purpose of the treated water dictates the priority contaminants and thus the suite of treatment technologies that must be deployed (i.e., fit-for-purpose). The chosen targets are surface (aquifer) discharge, disposal well injection, reformulated fracking fluid, agricultural reuse for non-consumable crops, livestock watering, and potable water.

The values reported in Fig. 4 (further details in Table S2) should be viewed as general guidelines (U.S. EPA, 2016b). As detailed below, robust approaches are desired, but a single unit with the capability to handle all possible contaminants over the potential concentrations is not realistic. Instead, flexible and modular technologies that preferentially target specific classes of contaminants must be engineered. When possible, multifunctionality – defined here as the ability to simultaneously treat different classes of pollutants that would traditionally require different (sequential) processes or conditions – is also desirable. Practically, multifunctionality manifests through technologies that can bridge the gap between the traditional treatment stages outlined in Fig. 3.

Regarding Reuse, quality standards for O&G reservoir flooding or fracking fluid water are not formally established. Rather, requirements are company- and/or site-specific and loosely defined.



**Fig. 4.** Final treatment goals for disposal (surface discharge and disposal well); reuse (fracking fluid); and recycle (agriculture, livestock, and potable water) end-uses according to ten contamination metrics. The average concentration values, and standard deviation, of U-PW contaminants from Fig. 1 are shown in shaded gray. Tabulated data are presented in Table S2.

For example, recent technical developments emphasize the use of friction reducers that tolerate remarkably high TDS ( $>300,000 \text{ mg L}^{-1}$ ) environments (Sareen et al., 2014; Zhou et al., 2014). This has resulted in the rise of “slickwater” and, more recently, “high salt tolerant gel/cross-linked gel” fracs (Barati and Liang, 2014; Palisch et al., 2010). With advanced friction-reducers, reuse is possible at TDS levels that are one order-of-magnitude higher than was feasible less than a decade ago (Acharya et al., 2011). Aside from TDS, operators will also prioritize contaminants in the source water used for fracking fluids (e.g., iron, sulfate) depending on the chemical additives/formulation they intend to implement. To illustrate the implications of source water characteristics in the context of fit-for-purpose treatment, consider a simple example: recent work characterizing flowback water from DJ Basin (Colorado) reported TDS of  $22,500 \text{ mg L}^{-1}$ , TSS of  $360 \text{ mg L}^{-1}$ , a combined sulfide + sulfate concentration of  $1.6 \text{ mg L}^{-1}$ , and an oil and grease concentration of  $59 \text{ mg L}^{-1}$  (COD  $1218 \text{ mg L}^{-1}$ ) (Lester et al., 2015). If the intent is to reuse this water on-site for further HF activities, TDS, TSS, and sulfur species are all within a tolerable range for direct reuse. However, the organic load (i.e., oil and grease) would need to be reduced by a factor of  $\sim 2x$  prior to reuse, implying that treatment efficacy could be optimized by deploying technologies that selectively target these contaminants (discussed in Section 4.2). A key conclusion from this survey of treatment objectives (discussed further in *Research Needs and Outlook*) is that in-field reuse is the most achievable value-added treatment objective (i.e., excluding direct-injection disposal), which further supports the notion that the HF water cycle (Fig. 2) could be closed, or at least that local freshwater withdrawals would be significantly reduced, at many drilling locations. Technologically,

this could be best achieved *via* improvements in primary treatment technologies.

Regarding *Recycle* targets, the selected standards for potable water (Guidelines for Drinking-water Quality: Fourth Edition Incorporating the First Addendum, 2017; U.S. EPA, 2012b, U.S. EPA, 2003), agriculture irrigation (Ayers and Westcot, 1985; Olkowski, 2009; U.S. EPA, 2012b; Waldner and Loooper, 2007), and livestock feed (Ayers and Westcot, 1985; U.S. EPA, 2012b; Waldner and Loooper, 2007) are stringently defined. However, the bulk contamination metrics used here fail to capture the importance of some high-priority, low concentration contaminants (e.g., lead in drinking water) that would need to be addressed in a more detailed analysis. Amongst these recycle goals, arguably the most promising is for irrigation of non-consumable, salt-tolerant crops such as cotton (Lewis, 2015; Sabie, R., Jr., Fernald, A., 2016) wherein human exposure risks are greatly minimized. In general, however, a central conclusion from this analysis is that most *Recycle* targets require an order-of-magnitude reduction in several of the identified contamination metrics and therefore stand as the most technically and economically challenging end-uses. Specifically, *Recycle* goals are hampered by high concentrations of multivalent inorganic species (e.g., NORMs, heavy metals, sulfur species; Fig. 4d) which are the main targets of current secondary treatment options. A compelling motivation for emerging, next-generation technologies is to (1) offer methods with greater selectivity towards the removal of multivalent inorganic species and (2) bridge the gap between the function of traditional primary and secondary treatment purposes. In other words, deploy multifunctional primary treatment technologies that can offer the additional benefit of multivalent ion removal.

For Disposal, U-PW discharged to municipal treatment plants or disposal wells (designated “Class II injection Wells” in the U.S., U.S. EPA, 2012a) is regulated by the EPA, while surface discharge – although very rarely permitted – is regulated through a combination of national and sub-national policy (Texas Commission on Environmental Quality, 2016; U.S. EPA, 2016b). As discussed in Section 3.2 *Current Practices*, disposal injection is typically favored by operators in regions of the country that permit it, as the associated treatment requirements are comparatively minimal and therefore less expensive. Often, disposal injection requirements can be economically met after the current primary treatment steps alone.

When taken in context with the current treatment technologies employed for U-PW treatment, the situation that emerges is rife with opportunities for next-generation on-site treatment approaches (Alvarez et al., 2018). PW may be stored on site for up to several weeks before being managed, as throughput requirements (i.e., temporal treatment capacity) and operation mode (e.g., batch, continuous) can be remarkably flexible parameters depending on site logistics and local water infrastructure/availability. The following discussion highlights a variety of next-generation treatment technologies that hold promise for PW.

#### 4.2. Targeting organics and bacteria

In complex water matrices such as U-PW, few chemical or engineered technologies are available to selectively remove bacterial species and/or hydrocarbons from the perspective of cost-efficiency. To date, this technological shortcoming stands as the greatest barrier to in-field reuse objectives. Biocides are actively used to control microbial growth, but they inherently require consistent, repetitive dosing, regulations can limit their use, and they are challenged by the development of bacterial resistance (Singer et al., 2016; Xi et al., 2009). Moreover, the introduction of treatment chemicals (particularly chlorine-based biocides) presents the risk to form persistent and harmful contaminants (e.g., halogenated organics) (Krasner et al., 2006). This can be especially detrimental for many potential recycle opportunities outlined previously. While the organic content is a small fraction of the inorganic content (e.g., TDS) in PW, the exact nature and amounts of these compounds are rarely known prior to treatment. As a result, this implies that defining the “selectivity” of successful technologies is in fact a balance: approaches that target classes or types of compounds (e.g., aromatic hydrocarbons) will be more useful than those aimed at specific molecules (e.g., benzene).

Advanced Oxidation Processes (AOPs) are attractive for recalcitrant waters since they rely on the *in-situ* formation of highly reactive, non-selective radicals to degrade organic pollutants, holding potential to yield sterile brines without requiring physical separations (Fernández-Castro et al., 2015; Oller et al., 2011; Pera-Titus et al., 2004). AOPs are generally based on (1) photolysis (e.g., UV, V-UV), (2) hydrogen peroxide ( $H_2O_2$ ), (3) ozonation ( $O_3$ ), or (4) Fenton/Fenton-like processes (Pera-Titus et al., 2004). However, AOP operation costs often restrict suitable target waters to a COD (related linearly to TOC) below  $5000\text{ mg L}^{-1}$ , which is much lower ( $12\times$ ) than in some U-PW (Pera-Titus et al., 2004). Furthermore, efficacy of photolysis approaches are greatly inhibited by U-PW turbidity (up to  $1500\text{ NTU}$ ); and the near neutral pH (6–8) precludes Fenton chemistry which exhibits optimum performance around pH 3 (Moreira et al., 2017). A popular approach to improve AOP performance is to combine them with biological treatments. However, successful pilot-scale examples of AOP + biological treatments have been limited to milder environments (i.e., brackish waters, <3 wt% salts) with consistent effluents such as pharmaceutical, tannery, and textile wastewater (Oller et al., 2011).

Similar emerging technologies employing heterogeneous catalysis (Heck et al., 2019) have been recently demonstrated on the bench-scale to function even in high-salinity ( $TDS > 100,000\text{ mg L}^{-1}$ ) environments (Yin et al., 2019). As with traditional AOPs, catalytic technologies hold the ability to generate oxidative species *in-situ* and inherently avoid the generation of a separate, concentrated waste stream, albeit with the requirement of an additional chemical oxidant precursor. Similarly, although the practical utility of photocatalytic water treatment technologies has recently been subject to debate (Loeb et al., 2019), the possibility that PW might offer the precise type of niche application where engineered photocatalyst systems can flourish cannot be ruled out at this time.

The analogous Electrochemical AOPs (EAOPs) arguably hold even greater promise: the most fundamental being anodic oxidation (AO). AO processes can (1) directly oxidize organic pollutants *via* electron transfer and/or (2) indirectly oxidize organics through generated reactive species. While reactive oxygen species (ROS) are the most classically desired oxidants, bulk solution oxidants such as chlorine and sulfate/persulfate may also be generated beneficially (García-Segura et al., 2018; Moreira et al., 2017). For further degradation capacity, AO may be combined with the cathodic production of  $H_2O_2$  utilizing a porous gas-diffusion electrode (AO + cathodic  $H_2O_2$ ) (Barazesh et al., 2015). In theory, the  $Fe^{2+}$  found naturally in PW could also be utilized to harness Fenton chemistry (Electro-Fenton, EF) (He et al., 2019), though EF suffers from the same pH limitation as its conventional analogue (Moreira et al., 2017). Similarly, photolysis-enhanced EF methods still display poor performance in turbid waters and high cost inhibit implementation.

Despite these limitations, EAOPs (specifically AO and AO + cathodic  $H_2O_2$ ) hold great promise for PW since, as stated prior, native ionic species can form powerful oxidants (e.g., active chlorine) to degrade organics and/or act as a biocide (Ghanem et al., 2016). Furthermore, PWs have a mean conductivity around  $140,000\text{ }\mu\text{S cm}^{-1}$  and can exceed  $20\text{ S cm}^{-1}$  ( $3\text{--}400\times$  that of seawater) suggesting that EAOP efficiencies will not be hampered by charge transfer effects often observed in potential potable water sources. Nonetheless, these complex electrolyte mixtures also pose serious challenges: hydroxyl radicals can be rapidly scavenged by sulfate and chloride species, iron complexes (e.g., sulfato-iron and chloro-iron) can hamper Fenton reactions, and side reactions can generate additional toxic pollutants such as perchlorate and halogenated organics that would need further treatment (Chaplin, 2014; Radjenovic and Sedlak, 2015; Yin et al., 2018).

Other tailored engineered nanomaterials (ENMs) may also find opportunity to offer at least incremental improvements to current PW treatment methods. Specifically, the notion of multifunctional materials (e.g., combined adsorptive and photocatalytic materials) could bridge the gap between the traditional chemical and physical treatments (Alvarez et al., 2018). As a basic example, nano-adsorbents typically offer significantly higher specific surface areas and sorption sites than many established materials (e.g., carbon nanotubes vs. activated carbon) which can significantly increase the practicality of these materials in highly-contaminated matrices such as PW (Qu et al., 2013). In addition, the surface of these materials can be further modified to contain, say, antibacterial/antimicrobial particles (e.g., nano-silver) or active catalytic sites to oxidize or fragment (adsorbed) organics and bacteria (Alvarez et al., 2018; Qu et al., 2013).

#### 4.3. Targeting inorganic contaminants

Even free of bacteria and organics, PW end-uses (especially Recycle goals) are limited by remarkably high TDS

(>200,000 mg L<sup>-1</sup>), hardness and scale, as well as compounds containing iron, sulfate, NORMs, and heavy metals. Shaffer et al. provided one of the first thorough looks at promising desalination technologies for shale PW in 2013 (Shaffer et al., 2013). Reviewed were mechanical vapor compression (MVC), membrane distillation (MD), and forward osmosis (FO). All three have potential to be economical, but MVC is the most mature technology and the simplest to implement. MVC, which exploits the latent heat produced during the compression of vapor to generate additional energy for vaporization, is the current standard for desalination during steam assisted gravity drainage in heavy oil fields (an enhanced recovery technique) and industry expertise is already established. The modularized design of the evaporator lends itself well to the required flexibility; TDS capacity can be scaled with additional evaporator/condenser units. Two primary disadvantages of MVC are the relatively high energy cost associated with operation (~10.4–13.6 kWh/m<sup>3</sup> distillate) (Shaffer et al., 2013), and the need for a reliable electrical grid on-site. Improving MVC efficiencies is an ongoing research topic (e.g., material heat transfer, drop-wise distillation, etc.), but it should be considered that coupling this technology with EAOPs could help justify the capital investment for a power grid at remote locations.

More recently, a rigorous review of membrane-based technologies for applications in O&G PW was conducted by Chang et al. (Chang et al., 2019). Included in this discussion were high-pressure membrane processes (reverse osmosis [RO] and nanofiltration [NF]), osmotically driven membrane processes (forward osmosis [FO]), thermally driven membrane processes (direct contact membrane distillation [DCMD]), electrically driven membrane processes (electrodialysis [ED], electrodeionization [EDI], capacitive deionization [CDI]) and more (including microbial capacitive desalination/deionization and vacuum membrane distillation). While a detailed overview of each of these processes is beyond the scope of this review (and would be redundant), a discussion can offer an additional perspective on how best to implement these technologies in the context of establishing fit-for-purpose technologies.

A key shortcoming of membrane technologies is the large capital and operation costs associated with treating complex, high salinity feeds and the relatively low water recovery rates (~50%) that are evident in most tests with real (i.e., non-synthetic) PW. In the pursuit of many recycle goals for which the concentration of key contaminants must decrease to ppm/ppb levels (e.g., heavy metals in drinking water), the prospect of high reject could be tolerated for the sake of a high purity product water. However, if the intended end-use is to reuse PW on-site many (if not most) state-of-the-art membrane technologies do not serve to resolve the issues that currently hinder oil-field operators. High-cost, low-recovery treatments which generate additional, now more concentrated, waste streams do little to prevent the need for off-site transportation and in most cases will struggle to find economic viability. Moreover, from an environmental perspective, it cannot be asserted at this time that minimizing the volume of disposed water at the cost of greater waste severity (i.e., contaminant concentrations) is an improvement over current practice.

This is not to say that membrane-based technologies should not be employed in PW reuse applications, but rather that research in this area would benefit from modifying the current metrics of success. Considering that reuse applications can generally tolerate relatively high (>70,000 mg L<sup>-1</sup>) TDS concentrations (e.g., chlorides, alkali/alkaline-earth metals), but are often less tolerant of specific inorganic species such as iron (precipitates such as iron oxides and iron sulfides can damage drilling equipment) or boron (borate crosslinking with gel fracturing fluids) the prospect of engineering membrane-based technologies with greater ion

specificity (i.e., secondary treatment options) could provide an invaluable tool for operators.

Another promising avenue for targeting dissolved and suspended contaminants is electrocoagulation (EC) (Garcia-Segura et al., 2017). EC utilizes a sacrificial anode (iron and/or aluminum) to release active coagulant precursor ions into solution while gas evolves at the cathode (typically H<sub>2</sub>) (Holt et al., 2005). It has historically been used to target hardness, heavy metals, oil and grease, and other organic substances in a wide array of wastewaters (including recent examples in the O&G industry (Da Costa et al., 2016; Ringer et al., 2017), but has failed to find lasting commercial application (Esmaeilirad et al., 2015; Holt et al., 2005; Zhao et al., 2014). This method is advantageous in that treatment can be performed with low capital cost, minimal maintenance, and natural settling can serve as the primary separation mechanism. EC has the key benefit of being largely non-selective towards contaminants, thus fulfilling the requirement for a robust technology, while also being modular enough to implement alongside other treatment technologies (e.g., E/AOPs). An added advantage is that electrochemical redox processes are triggered to form hydroxyl radicals, chlorine gas and related oxidants for killing bacteria *in-situ* (Fedotov et al., 2013). Unfortunately, specific high-priority contaminants for HF reuse (e.g., boron) may not be practically addressed by EC alone (Chorghé et al., 2017), further emphasizing the need for flexible, modular technologies and treatment trains (Zhao et al., 2014). Additional limitations to the technology include scalability, and the need for routine manual intervention to replace electrodes and/or clean the equipment to prevent fouling. However, EC still stands out as a notable technology in terms of multifunctional capabilities; EC (or similar technologies) could bridge the gap between late-stage primary treatments (e.g., coagulation, and floatation and clarification) and secondary treatment (e.g., multi-valent ion removal). A related technology called *Magnetic Ballast Clarification* has been recently reported to use a combination of coagulants and flocculating polymers in the presence of magnetic particles to clarify U-PW at rates up to 5 gal min<sup>-1</sup> (Ringer et al., 2017). U-PW and the magnetic particles are introduced into the process unit with agitation resulting in the magnetic particles being coated with the polymers, surfactants and charged species. A magnetic separator near the water surface then captures the contaminated magnetic particles for cleaning. Note also that EC treatment will inherently generate a sludge that can potentially contain high levels of heavy metals, NORMs, sulfur, and toxic chemicals. While a discussion of regulations is beyond scope, it is safe to assert that EC will necessitate the handling and transportation of solid material offsite. To date, the environmental and economic impacts of this practice remain largely unexplored.

Finally, although it is the least mature of the technologies discussed here, reductive heterogeneous catalysis is a promising emerging method to selectively target oxyanion contaminants, in addition some small halogenated organics (Heck et al., 2019; Yin et al., 2018). In a similar engineering approach to AOPs, Advanced Reduction Technologies (ARTs) operate through the *in-situ* reduction of the target contaminant, but with distinct difference being the requirement of a reductant precursor. This stands in contrast to the previously discussed physical separations for inorganic contaminants that inherently generate additional waste streams. The general principle of heterogeneous catalysis-based ARTs is to transform the toxic compounds into benign products which – depending on the targeted end-use of the treated water – do not necessitate additional removal.

## 5. Research Needs and Outlook

The literature severely lacks case studies that focus on U-PW

treatment. The body of research is growing, but most publications to-date emphasize desalination exclusively despite a minimal need to remove the most abundant ions (e.g., Na<sup>+</sup>, Cl<sup>-</sup>) for HF reuse opportunities. A primary objective of this work is to highlight end-uses that can tolerate relatively high salinity provided that bacterial and organic content are minimized. Aside from evaluating performance in “real” waters, a thorough investigation of the interplay and possible synergy between treatments is necessary. Several methods discussed here appear promising for U-PW, but case studies must be performed before industry will be willing to invest in high-risk, emerging technologies. In addition, more rigorous reporting of total PW volumes, as well as the subsequent management practices of that water, would greatly benefit the professional and scientific community surrounding this issue.

As with the example of elevated contaminants in EC sludge, there are still many uncertainties regarding the potential toxicity and long-term consequences of U-PW reuse activities. Given our current understanding of U-PW management, the prospect of implementing the massive volumes of U-PW that are currently disposed of towards reuse/recycle opportunities warrants the attention of the scientific community. However, deploying decentralized treatment activities of this scale will be a novel task for industry and the volume/severity of the waste generated from U-PW treatment must be carefully weighed against the environmental benefit of reducing freshwater withdrawals. Furthermore, reuse goals should be prioritized over recycle. For relatively high-quality U-PW, some recycle options – such as crop irrigation – are viable targets. In one example, Texas A&M in collaboration with Anadarko Petroleum successfully grew cotton in western Texas using treated PW (Lewis, 2015). However in most cases, the feed more closely resembles that of seawater, and technologies for this application necessitate a separate discussion. Regarding recycle options that involve direct human interaction/consumption, there are still many uncertainties pertaining to the identity and potential toxicity of the organic compounds (Butkovskiy et al., 2017). For the general discussion presented here, bulk metrics for organic content (e.g., COD, TOC) are appropriate, however the reactivity and fate of many chemicals used in fracking fluids is not fully understood when it comes to potential human health effects.

Among the newer technologies, EAOPs (particularly AO and AO + cathodic H<sub>2</sub>O<sub>2</sub>) require the development of efficient, chemically resistant electrodes. A formalized understanding of catalytic structure–property relationships under these conditions must be proposed before materials can be engineered that are resistant to chemical poisoning and selective towards the desired oxidant. Similarly, a major obstacle for EC technology is electrode passivation. Future research must elucidate the passivation mechanisms in this class of waters and engineered solutions to reverse or prevent the process (es) is needed.

Desalination research is a rich field, and the technologies discussed here should not be considered comprehensive, however there is a distinct void of technologies that can *economically* operate in complex matrices at TDS levels surpassing ~100,000 mg L<sup>-1</sup>. While many membrane-based technologies have been investigated in recent years, the inevitable occurrence of membrane fouling (e.g., colloidal, scale, bio-, organic fouling) coupled with membrane degradation continue to limit commercial applications. Broadly, complex water matrices such as PW provide opportunities for innovative multifunctional materials such as adsorbents decorated with antibacterial nanoparticles, or membranes embedded with active catalysts that can minimize biofouling through *in-situ* generated oxidants. Finally, although likely far from commercial viability, emerging ARTs will benefit from a continued investigation into the molecular-level structure–activity relationships of nanoparticle catalysts. There is currently a great need to discover new

approaches to both improve selectivity and, perhaps more importantly, prevent poisoning by benign ionic species; further, a departure from precious metal-based materials may be necessary for economic viability.

## 6. Conclusions

Overall, fracking is poised to be the cornerstone of U.S. hydrocarbon production for the foreseeable future. The enormous volumes of variably contaminated waters derived from these operations are a mounting environmental and economic risk, necessitating new management practices for industry. U-PW management has proven to be a unique technological challenge. There is no standard approach to U-PW treatment due to the issues associated with the elevated concentrations of TDS, organic compounds, bacteria, iron, sulfur species, and NORMs. U-PW is a research target with immense societal impact, but it is so far relatively overlooked by the scientific community. We hope is that this publication will enhance appreciation for the scale and scope of this issue, and promote the development of fit-for-purpose treatment approaches (enhanced by higher selectivity for efficient removal of specific pollutants of greatest concern, and by multifunctionality to simultaneously remove different classes of pollutants that require different treatment processes) to enhance the cost-effectiveness of produced water reuse.

## 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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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115467>.

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