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Produced Water Reuse and Research Needs Outside Oil and Gas Operations

MODULE SUMMARY

The objective of Module 3 is to promote an informed dialogue on current and future reuse of produced water outside oil and gas operations. It examines the drivers for reuse and aims to define the information necessary for knowledgeable decision making by regulators, industry, and other stakeholders. It also provides insight on how to fill identified research needs.

Reuse of produced water outside oil and gas operations could take various forms. Potential options for the treatment and reuse of produced water outside the oil and gas industry can be sorted into three primary categories: land application (e.g., irrigation, roadspreading), introduction to water bodies (e.g., discharges to surface water, injection or infiltration to ground water) and other industrial uses (e.g., industrial feed streams, product or mineral mining). Some options, such as surface water discharge, are active in limited circumstances today. Others, such as utilizing treated produced water in other industrial systems, are under investigation or theoretical.

Drivers for considering produced water reuse differ for industry and other stakeholders. States and regulators may be driven to investigate reuse for reasons ranging from drought and groundwater depletion to disposal-related induced seismicity. For the oil and gas industry, operational and economic considerations, such as a reduction in nearby cost-effective disposal capacity, may drive a search for produced water management alternatives including reuse.

For the majority of anticipated reuse scenarios, produced water will be treated before reuse, using a “fit-for-purpose” approach. Produced water quantity and quality is not uniform, and neither are the circumstances of its potential treatment and reuse. Under a “fit-for-purpose” mindset, research, treatment decisions, risk management strategies, and in some cases even approval processes should be tailored to address a particular produced water for a particular type of reuse. Not all reuse scenarios will require the same analysis or approach.

Treatment can take many forms, and the particular treatment utilized will depend on the desired quality needed to support the intended end use. Designing an appropriate treatment train will play a vital role in reducing potential risks to health and the environment. Treatment of produced water for reuse objectives that demand consistent high quality can present unique challenges such as managing variability; significantly reducing high total dissolved solid levels, difficult-to-treat organic constituents, and naturally occurring radioactive material; and handling residuals.

Potential risks to health and the environment must be well understood and appropriately managed in order to prevent unintended consequences of produced water reuse. Research objectives will also be “fit for purpose.” The traditional mechanisms for produced water management and disposal (namely underground injection) have not
previously demanded a substantive understanding of the character of produced water or the risks of its intentional treatment and reuse or release. As reuse opportunities are assessed and decisions are made, advancing knowledge and understanding of produced water and potential risks to health and the environment from its reuse outside oil and gas operations is necessary to inform the development of protective programs. These research and data collection efforts should be “fit for purpose” similar to treatment technologies, as the questions and information necessary will be specific to the particular produced water and reuse scenario envisioned.

**Beyond managing health and environmental risks, other challenges must be weighed in determining the feasibility of a produced water reuse program.**

Costs and risks related to potential reuse programs include legal and regulatory questions concerning authorization or permitting for reuse; understanding and managing public perception of the reuse program; logistical considerations relating to timing and necessary infrastructure; costs of treatment, transportation, and solids management; the potential need to adapt contractual commitments; fluctuations in energy supply and demand; market-related costs or opportunities; and water rights issues. Environmental considerations beyond direct health or ecosystem impacts include emissions from treatment, managing waste materials from treatment, cumulative ecosystem impacts, or other localized issues. Identifying benefits of reuse proposals—such as a greater ability to meet the needs of downstream water users or a reduction in disposal-related seismicity—allows trade-offs for different reuse opportunities to be considered.

**Data and information currently available may not be adequate to support reuse programs that protect human health and the environment with an acceptable level of certainty.**

Unknowns or uncertainties regarding produced water and specific risks related to its treatment and reuse can make decision-making difficult. Strategic advancements in data and analysis are needed to inform risk-based decisions and support the development of reuse programs that are protective of human health and the environment. Produced water can pose challenges in assessing feasible reuse options, including complex chemical character, analytical limitations, variability, and limited applicable permitting or regulatory structures, among others. In order to better support future opportunities for reuse, working collaboratively toward addressing such challenges in the near-term is vital.

**Risk-based decision-making concepts can be applied to assist decision-makers in assessing and reducing risks associated with a given reuse scenario.**

Incorporating the traditional concepts of risk-based decision-making – research, risk assessment, and risk management – as applied to the unique nature of produced water treatment and reuse, this module presents a conceptual framework designed to assist decision-makers in evaluating a given reuse scenario. GWPC does not intend to prescribe a singular or set process for assessing individual reuse proposals. Instead, GWPC expects this effort to spur discussion, encourage collaboration, promote targeted research, and further multi-stakeholder engagement surrounding this important issue, including refinement of the framework itself.

The phases of the framework include:

- **Phase I: Preliminary assessment of the proposed program** to determine whether the reuse scenario is likely to be feasible and if additional analysis is worth investment. A basic screening compares known characteristics of the produced water to expected water quality needs and reviews, practical considerations such as public perception, regulation, logistics, economics, and benefits, to decide whether the program merits further in-depth analysis.
MODULE 3

• **Phase II: Identification of stressors of interest for treatment and risk analysis.** (A ‘stressor’ is simply something that can induce an adverse response – in the context of produced water, this might be a constituent of concern or the mixture itself.) This phase has two key objectives: (1) adequately characterizing the produced water to identify stressors of interest that should be targeted for analysis and potential, reduction, or removal; and (2) decision-making and assessment regarding the selection or development of appropriate treatment technologies. The understanding of influent quality, treatment capabilities, and effluent quality narrows the scope of Phase III analysis to priority constituents of concern.

• **Phase III: Risk assessment – treated produced water.** Using knowledge obtained in Phase II, a traditional risk assessment model is applied to treated produced water, to identify risks to human health or the environment that must be reduced or otherwise managed. This phase assesses potential exposure pathways (e.g., through building conceptual site models) and determines whether and at what magnitude a particular constituent or the mixture of treated produced water itself may lead to adverse effects.

• **Phase IV: Risk management and decision making.** Based on the data, tools, and technologies identified in previous phases, an informed decision is reached as to whether and how to move forward with a project, including defining the necessary risk management strategies. It includes a final evaluation of the “practical considerations” of Phase I, a decision on whether the risks as characterized are expected to be manageable, an opportunity to incorporate advanced or additional treatment options, and an effort to implement or develop appropriate risk management strategies, such as quality standards and permit limitations, monitoring tools, best practices, and information sharing. While Phase IV moves toward implementation of a reuse program, it also recognizes the importance of a process of continuous learning and incorporation of new knowledge or tools.

Identifying specific reuse options that address current or emerging needs or drivers in specific regions is an important next step in prioritizing research and development.

Focusing on specific reuse options in specific regions based on the produced water potentially available and need for nearby water users will enable time and resources to be invested in purposeful and actionable research and development with a more defined set of facts and circumstances.

Expanding knowledge and tools for produced water characterization, treatment, risk assessment, and feasibility for reuse is a growing area of focus for research and development.

In addition to substantive discussion regarding research needs related to better characterizing produced water and assessing and managing risks, this module includes an overview of various treatment technologies that exist or are being actively researched. The economic treatment of produced water is a critical step in achieving a feasible project that meets quality objectives, and interest in developing, testing, piloting, or implementing various technologies spans the academic, government, and industrial spaces.

Published literatures is available that can help guide future reuse evaluations.

This module involved a literature review with a defined scope and timeline that identified hundreds of potentially relevant papers and aimed to summarize the types of available texts and learnings at a very high level. In the future, a more targeted literature review may be a useful component of an initial assessment of a particular reuse project or scenario.
Background
The objective of Module 3 is to promote an informed dialogue on current and future reuse of fit-for-purpose produced water outside oil and gas operations. It examines the drivers for reuse and aims to define the information necessary for knowledgeable decision making by regulators, industry, and other stakeholders. It also provides insight on how to fill identified research needs.

Operators and regulators alike are beginning to rethink the economics and long-term sustainability of traditional produced water management practices. While most near-term alternatives focus on recycling produced water for operational uses to reduce fresh water consumption in oil and gas operations (as discussed in Module 2), interest is growing in the potential for produced water reuse outside the oil and gas industry. Unique conditions in oil and gas operations — such as remote locations, dispersed water production, and high salinity levels — have historically made some produced water reuse options difficult to accomplish. In addition to these challenges, produced water reuse potential often comes with complex scientific, regulatory, and policy considerations, specifically with respect to risk management.

Before alternative management strategies can be broadly implemented, a more holistic understanding of the risks and benefits is necessary. This module provides a high-level overview of the types of questions that need to be considered, homing in on components of the research and development (R&D) process for treated produced water reuse outside oil and gas operations. Together with academia, industry, regulators, and non-governmental environmental organizations, GWPC has developed a detailed overview of some top-level considerations and research needs on this subject. The aim of this effort is to identify priority questions or research objectives, and to describe the type of work that may need to be completed by a wide range of stakeholders to answer those questions.

While important questions remain to be addressed, produced water reuse is a subject on which research is rapidly advancing. This module includes a substantive literature review that covers published, peer-reviewed material, referencing other reports where applicable. The review includes selected studies on two types of produced water that are outside the scope of this report: produced water from coalbed methane (CBM) production and from offshore oil and gas production. Because offshore production has historically involved the assessment and permitting of produced water discharges to the ocean, lessons from offshore literature, permits, and practices warrant consideration to inform efforts onshore.

Produced water is not uniform, and neither are the circumstances of its potential treatment and reuse. While some broad research endeavors have value in advancing reuse (i.e., development of more economic treatment technologies; prioritized analytical method advancements), targeted assessments evaluating site-specific reuse options are expected to provide the most value in the near term. This module emphasizes the need to approach produced water reuse challenges and objectives with a fit-for-purpose mindset, meaning that research, treatment decisions, risk management strategies, and in some cases even approval processes should be tailored to address the reuse of a particular produced water for a particular type of reuse. It aims to present a useful framework for identifying and mitigating risks and other considerations as applied to a specific reuse opportunity being considered.

One substantive source of information on produced water and available data and literature on its character, treatment, management and other aspects is the USEPA report on “Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States” published in 2016. The report included two relevant chapters on “produced water handling” and “wastewater disposal and reuse” that contain an overview of information available as of writing of the report as well as an overview of data gaps and limitations in EPA’s assessment.
The scope of this module addresses produced water from onshore conventional and unconventional oil and gas production. Produced water includes water that flows back during and after the hydraulic fracturing process as well as formation water that returns over the life of a well. Only where it is important to differentiate between these two will this report do so. In most scenarios for discharge or reuse outside the oil and gas industry, the water being considered is most likely the water produced following the initial flowback phase, which would include primarily formation water.

Drivers for Reuse Outside Oil and Gas Operations

Drivers and Opportunities for States and Regulators

All regions of the country have unique characteristics. However, one common thread is the need for safe and adequate water resources to support local and regional needs. Water regulators are often looking for options that can help augment existing resources or slow the drawdown of aquifers or surface water sources without negatively impacting source water or wellhead protection areas. There are several reasons why regional leaders and decision-makers may investigate the role treated produced water may play in meeting water demands.

- **Drought and the demands of expanding populations.** Drought has become an increasing concern for large portions of the United States. The need for an adequate quantity of water for the environment, agriculture, industrial uses and drinking water is vital for public health protection, quality of life, and economic development. This need is particularly pressing where population and development expansion are occurring in regions where water resources are stressed or limited. As discussed in Module 2, reuse of produced water to replace water use in oil and gas operations may increase water resources locally available for other needs like agricultural, industrial, or municipal use. Outside oil and gas operations, produced water may potentially be treated to serve as an adequate substitute for fresh water, though in many cases current research needs to be further advanced to better inform those decisions and address quality and treatment considerations.


up potable water resources for higher quality water needs such as drinking water.

• **Fresh groundwater depletion.** In the United States, groundwater is the source of drinking water for about half of the total population, and in 2010, it provided over 50 billion gallons per day for agricultural needs. This heavy reliance on groundwater as source water in areas where groundwater withdrawal occurs at a faster rate than recharge is not sustainable. For example, the Ogallala Aquifer, which spans numerous states, has been severely depleted in the past half century (Figure 3-2). Depletion can reduce groundwater quantity and/or quality; reduce surface water quantity and/or quality in streams, lakes and wetlands where hydraulic connectivity exists; increase pumping costs; increase land subsidence; increase salt water intrusion; and, in some localized circumstances, cause movement of contamination plumes. Where feasible, use of treated produced water or even marginal quality groundwater in place of fresh groundwater could prove beneficial. Additionally, research and treatment could eventually support the utilization of this water in a way that restores certain aquifer volumes, such as through aquifer storage and recovery or managed aquifer recharge, though these alternatives require further analysis.

• **Surface water availability.** As with groundwater depletion, lack of surface water has led numerous municipalities and industries to seek alternative sources of water. Securing safe and reliable alternate sources of water that allow greater conservation of fresh water has the potential to provide increased operational flexibility and better cost management. Fit for purpose produced water could potentially serve as an additional resource option for municipalities or other industries that rely on increasingly limited surface water resources, may be able to restore wetlands negatively impacted by overuse, or could help maintain ecological flows in surface water bodies through treatment and discharge.

• **Induced seismicity.** Disposal of produced water through deep well injection has been the subject of much discussion and study due to the marked increase in the number of earthquakes occurring in some areas of the United States, with many believed to be induced rather than naturally occurring. In some circumstances, this increased seismicity is occurring in areas that are water stressed. Oklahoma is a prime example, where this added pressure on existing produced water resources...
management strategies, in addition to drought planning, is driving heightened consideration of reuse options.\textsuperscript{103}

- **Water planning goals.** Many states are committed to comprehensive or regional water planning studies. As these plans become more inclusive of all water sources rather than the traditional freshwater sources (i.e. shallow groundwater and surface water), it is likely that marginal quality water, produced water, municipal and industrial wastewater, and stormwater will be increasingly considered as potential alternative water sources in the future. To date, most of these plans (where they mention oil and gas development at all) focus on reducing fresh water volumes used in E&P operations. However, some are extending consideration to produced water as a resource for use within the oil and gas industry or potentially available for other purposes. For example, two of the four goals outlined in the water plan for the Red Hills Region of Kansas relate to produced water.\textsuperscript{104} Goal three calls for a reduction in the amount of freshwater used in oil and gas completion operations by 4 percent annually and goal four prioritizes work with the oil and gas industry to have 10,000 barrels of fresh water per day replaced with recycled water by 2040. In another example, Oklahoma developed a comprehensive water plan in 2015 that included recommendations for the development of best practices for energy and industry water use and promoted industrial use of marginal quality waters.\textsuperscript{105} The plan led to the creation of the Produced Water Working Group (PWWG) to evaluate current practices and potential uses of produced water. The PWWG published a report in 2016 which found that reuse for oil and gas production was the most economical near-term alternative for the state and pointed to treatment costs and other research needs (i.e., toxicological risks, water quality targets, potential beneficial uses) as areas for research and development for the longer term.\textsuperscript{106}

**Drivers and Opportunities for Industry**

As discussed in Module 2, produced water is widely used within the oil and gas industry, both in conventional plays for enhanced oil recovery (i.e., waterflooding) and in unconventional plays for completion activity (hydraulic fracturing), as an alternative to disposal. However, several operational and economic considerations within the oil and gas industry are driving decision-makers to evaluate produced water reuse outside the oil and gas industry as an additional water management option.

- **Limits to reuse in operations.** Over the last decade, the oil and gas industry has made great strides in finding ways to reuse produced water in hydraulic fracturing operations. However, reuse within unconventional plays is likely to have its limits, and this forecast is driving investigation of reuse or discharge opportunities elsewhere. Industry reuse becomes limited as new nearby completions decline, reducing or eliminating the need for water resources for well completion. This can occur when an area is fully developed, or for other reasons, like a commodity price downturn that results in slower development and fewer new completions. In these scenarios, the operator is still generating produced water at active wells but has limited or no nearby operational reuse. When this happens, operators are currently most likely to increase their use of nearby underground injection wells or consider the need for additional disposal wells. Historically, the oil and gas industry has used nearby Class II Underground Injection Control (UIC) wells for disposal of the produced water or has relied on re-injection to produce more oil from water

\textsuperscript{103} Earthquakes in Oklahoma: What We Know, \url{http://earthquakes.ok.gov/what-we-know/}; Oklahoma Water Resources Board, Water for 2060 Produced Water Working Group, \url{https://www.owrb.ok.gov/2060/pwwg.php}.

\textsuperscript{104} Kansas Water Office, Red Hills Regional Advisory Committee Action Plan, \url{https://kwo.ks.gov/about-the-kwo/regional-advisory-committees/red-hills-regional-advisory-committee}.

\textsuperscript{105} The Oklahoma Comprehensive Water Plan, Oklahoma Water Resources Board, \url{http://www.owrb.ok.gov/supply/ocwp/ocwp.php}.

flood operations. However, as the economics and capabilities of advanced treatment technologies improve, there are increasing opportunities to look for other management or reuse options.

- **Limited disposal availability.** Disposal issues vary depending on region and geography. In some places, challenges may arise from pressure imbalances, capacity limits, or induced seismicity-related constraints on available injection and disposal formations, particularly during times when completion and associated flowback activity is high. In other places like Pennsylvania, suitable disposal zones are simply not available or economically accessible and the number of UIC wells are limited. As a result, most produced water is either reused for ongoing operations, trucked long distances to neighboring states for disposal, or, in more limited circumstances, treated for discharge. In such scenarios, where traditional options for produced water disposal are increasingly limited or face significant constraints, the economics of disposal and treatment may change, creating a potential for advanced treatment that had to-date been considered too costly in most parts of the country. Along with looking for ways to expand disposal availability, increased reuse of produced water – within or outside oil and gas operations – may be part of the solution to limited disposal availability in some regions.

- **Economic considerations.** The economics of water use in oil and gas operations can be most simply stated as “how much does it cost to acquire source water and how much does it cost to dispose of produced water or otherwise manage it?” At the beginning of most oil or gas developments, the most economically viable water management strategies are sourcing water locally and disposing of produced water into nearby permitted injection wells, if available, or using it in enhanced oil recovery or waterflood operations. As development in plays continues, infrastructure construction (e.g., pipelines for gathering and transporting produced water, as well as storage and treatment facilities) and increased volumes of produced water make the economics of reuse in subsequent completions more attractive, particularly in circumstances where the cost

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to obtain source water increases. Over time, however, it is possible that disposal capacity and reuse within oil and gas operations may become constrained in some areas, prompting a new set of economic options: investing in new injection and disposal zones, spending more on advanced treatment like desalination to allow reuse or discharge of produced water outside operations, or shutting in producing wells (though the latter option is less likely). With research and development advancements, it is possible that future economics could support large-scale reuse outside oil and gas operations where the water quality and environmental challenges can be met by advanced treatment technologies. This research and development may also take into consideration economic opportunities and co-benefits potentially associated with advanced treatment of produced water, such as recovery of saleable products like salt, heavy brine, iodine, or lithium.

Natural Gas Supply Collaborative: Environmental and Social Performance Indicators. Stakeholders can sometimes drive adjustments in practices or decision-making. For example, the Natural Gas Supply Collaborative (NGSC)—a voluntary collaborative of natural gas purchasers (including Austin Energy, Pacific Gas and Electric, and Xcel Energy, and Consolidated Edison)—published a report in 2017 identifying non-financial performance indicators related to protecting the environment and local communities in the production and supply of natural gas. The report called for reporting on these indicators, a number which relate to water, including:

- Sourcing of water for completions,
- Strategy for managing fresh water use, and
- Strategy for managing water onsite and wastewater.

Relevant leading practices highlighted include:

- Reducing freshwater use through efforts such as wastewater recycling,
- Use of brackish water, and operational improvements;
- Not using local freshwater resources that directly compete with, and negatively impact other, local uses, such as agriculture and drinking supplies;
- Describing how wastewater is handled and its ultimate disposition; and
- Participating in research to better understand opportunities for reuse outside the field and the health and environmental risks associated with reuse, especially for agriculture, prior to its reuse offsite.

For the leading practices, the NGSC referenced similar indicators in other frameworks, including GRI, IPIECA and API. See https://www.mjbradley.com/content/natural-gas-supply-collaborative-0.

While there are clear drivers for the reuse of treated produced water outside oil and gas operations, additional considerations must be addressed to understand and mitigate potential risks and promote smart decisions. This section introduces the challenges and opportunities pertinent to decision makers in evaluating new options to reuse of produced water.

Why Is Research Needed?

The potential to beneficially reuse treated produced water outside oil and gas production presents opportunities and prospective benefits for end users, as well as for the oil and gas industry itself. However, challenges associated with produced water may make decisions regarding its reuse complex. Research to address these challenges may be appropriate to support expanded reuse efforts in the future. For example:

- **Analytical challenges and limitations.** Produced waters lack reference materials, essentially a ‘control’ for a type of sample or mixture, which is either used to calibrate instruments for chemical quantification or to validate methods between labs and estimate error. Some complex waste streams or types of environmental samples also have associated matrix reference materials, which allow analysts to account for chemical or matrix interference from the sample media. The lack of references, as well as produced water variability generally, can pose a challenge in both verifying and standardizing produced water analyses as well as setting the appropriate regulatory goals for new uses. A lack of matrix reference materials is particularly problematic for produced water, which often exhibits matrix interference due to its high salinity. Beyond reference materials, produced water also includes a wide range of constituents for which standard analytical methods (e.g., those that are approved for use in a regulatory context) may not be available. While analysis of treated produced water presents fewer analytical methodology challenges—and therefore fewer method development challenges—there exists a need to demonstrate treated effluent assessment and monitoring is appropriate given an adequate understanding of the constituents in the influent. Identifying priority analytical advancement needs to appropriately assess the quality of produced waters proposed for reuse is a key opportunity moving forward.

- **Quantity of produced water available.** Although some states require volume reporting, widespread available data on produced water volumes is currently limited. In some areas, the large quantity of produced water that may be available could present compelling opportunities for fit-for-purpose reuse. However, absent improved data availability, the amount of produced water available may be difficult to predict and while operators

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115 For example, California’s Public Resources Code §3227 requires quarterly reports on all water produced, injected, and used within oil fields to the Division of Oil, Gas, and Geothermal Resources. Reports are aggregated and made available to the public, https://www.conservation.ca.gov/dog/58%20281/Pages/58_1281DataAndReports.aspx.


may have good internal volume predictions, that information may not be publishable or accessible. Limited data on produced water volumes and current management strategies also limits the ability to identify pressure points on existing disposal options in advance or to identify volumes that may need other management options, such as reuse. This makes it more challenging to pinpoint areas where targeted near-term research in support of reuse is needed.

- **Quality of produced water.** Published, publicly available research on the chemical and toxicological character of produced water and potential impacts of various reuse scenarios exists, and is growing, but is not extensive (see State of the Science: Literature Review). Limitations in peer-reviewed literature can present a challenge in establishing the appropriate parameters for different reuse options. There has been little historic need to conduct extensive studies to gather this data because traditional disposal methods, like underground injection, come with limited exposure pathways and demand little chemical characterization. EPA’s recent study of the hydraulic fracturing water cycle included a review of available publications on characterization of produced water and compiled a table of 599 identified water constituents, though the list was national. Specific studies do exist, data are often limited to regions where samples are readily available for study, like the Marcellus, and those studies are unlikely to be appropriate for decision-makers to utilize in other regions. Before reuse outside the industry, most produced water will require removal of salts and other dissolved solids, metals and other inorganics, such as ammonia, organics (some at trace levels), and potentially naturally occurring radioactive material (NORM).

- **Variability over time.** Produced water quality and quantity can vary over time and geography. This variability can make decision-making regarding various reuse options complex, posing a challenge not only with respect to permitting and monitoring, but also for business decisions and long-term agreements to take or provide such a water resource. Available produced water volumes are likely to change over time and may only be available in usable quantities for brief periods relative to other resources or an end user’s needs. This variability may play a role in decision making by end users that require long-term and consistent volumes versus end users seeking only seasonal volumes. On the other hand, quality variability may also present an opportunity in some regions, where better produced water quality may lend itself to more economical treatment. This is an additional reason why it is critical to understand the efficacy of treatment processes and their ability to robustly manage influent variability.

- **Logistics considerations.** In order to support reuse in other industries or for other purposes outside oil and gas operations, produced

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water will need to be transported from the point of production to the point of treatment and eventually to the point of reuse. This may involve complex logistical considerations, including temporary storage and transport capabilities (e.g., pipelines, trucks) or other potential delivery mechanisms such as discharge or aquifer storage. These logistical considerations can also increase the potential for unintended releases and associated risks. Infrastructure and conveyance decisions will be site or project-specific and the remote nature of many oil and gas production locations may play a role in determining the appropriate mechanism (i.e., surface discharge v. pipeline).

- **Permitting and regulation.** Existing permitting and regulatory structures are in many cases not written with these reuse scenarios in mind, as discussed in Module 1. Where regulatory programs may be required but do not yet exist or require update or modification, collaboration with regulatory bodies to identify appropriate standards will be necessary and should occur early in the decision-making process.

### When and Where Should Research Efforts Be Focused?

Some circumstances are likely to lead to discrete scenarios where research on new produced water management options should be prioritized. A substantive evaluation of risks and decision-making on a reuse project may take significant time and resources for operators, end users, and regulators. Understanding where and when to focus these efforts will be vital in ensuring that research is completed in a way that is timely, relevant, and actionable. Examples of scenarios that may call for research prioritization, particularly where more than one of these drivers overlap, include:

- Where produced water volumes are expected to exceed disposal capacity and/or volume demands for recycling in new completions;
- Where high produced water volumes overlap with high volume users of either fresh or saline water or with areas of freshwater scarcity relative to demand;
- Where produced water quality may require less treatment for the designated usage;
- Where projected local water demand exceeds reliable future supply; or
- When other drivers make investment in research, technology, and implementation more realistic or timely.

Identifying when and where research demands prioritization in line with the above examples is an important near-term research need. In some cases, additional data gathering, analysis, and modeling may be useful in identifying specific opportunities.

A logical initial exercise is to determine where areas of significant produced water volumes overlap with localized areas prone to water stress with large-volume users of either fresh or saline waters. A step further might involve a rough characterization of produced water quality relevant to water quality needs for other nearby users. Resulting maps or databases may be able to point to, for example, where high-volume production of a low-TDS produced water overlaps with significant nearby water withdrawals or demands for other uses. This exercise could help to prioritize, at least regionally, where more in-depth research on risks and opportunities for reuse may be most practical and actionable. This recommendation is in line with those of other collaborative efforts. One example is the Colorado Water Resources Institute’s Produced Water Workshop in 2006, where a key proposed follow-up action was collaboration with USGS and the Bureau of Reclamation to develop a map highlighting overlap of potentially useable produced water quantities and other factors that could indicate feasibility of use, including infrastructure.

Resources of relevance in prioritizing reuse opportunities could involve a combination of data such as

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125 Colorado Water Resources Institute and Colorado State University, Produced Waters Workshop (April 4-5, 2006) at v, available at [http://www.cwi.colostate.edu/media/publications/is/102.pdf](http://www.cwi.colostate.edu/media/publications/is/102.pdf). For the most part, presentations and conversation at the workshop focus on CBM. Other summary recommendations of this group included evaluation of treatment technologies, addressing concentrated wastes, pilot and demonstration projects, and enhanced communication and collaboration.
those included in Figures 3-4 and 3-5. Together, these three data sets illustrate how the factors of water use, produced water availability, and produced water quality could be correlated to determine the most feasible areas/region for further research.

Figure 3-4: Water Use in the U.S., 2015
Map showing current water withdrawal volumes by user/industry, including fresh and saline water and surface and groundwater, which may be useful in identifying areas where there may be a large water need.
**Produced Water Quality Table (Table 2-4)**

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**Figure 3-5: Examples of Data on Produced Water Availability and Quality**

*Source: Figure 2-32 (Module 2, p. 72) and Table 2-4 (Module 2, p. 95)*

The map, “Injected Produced Water by County (bbl.) in 2017,” shows areas where large volumes of produced water may be available for other uses. The “Produced Water Quality Table,” gives basic quality parameters, such as TDS, which could assist in narrowing down locations where TDS is low enough that treatment to meet quality objectives may be more likely to be economical.
One example of this type of effort can be found in a recent study published by the Colorado School of Mines. The research team in this study looked specifically at counties in Colorado, estimating or analyzing produced water volume, produced water quality, irrigation demand, and economic feasibility of treating produced water to irrigation standards (as compared to commercial disposal). The team developed a decision matrix to compare quantity, quality, and demand parameters and then ranked counties to pinpoint optimal locations for potential produced water reuse. After this ranking exercise, six counties were analyzed in-depth and three counties were determined to have water supply, quality, and demand numbers that signal opportunity for reuse. Based on this analysis the researchers concluded that produced water could supply ~3% of the irrigation demand across the six counties studied. While the researchers highlighted this work as an opportunity to look at produced water as a resource, the team also emphasized that decision-makers should consider potential crop uptake of contaminants and degradation of soil quality before deciding to irrigate with produced water.

Figure 3-6: The Concept of “Fit for Purpose” as Applied to Levels of Treatment for Different Reuse Scenarios
Source: Adapted and modified from USEPA 2012 Guidelines for Water Reuse

“Fit for purpose” commonly describes the level of treatment applied to a water in order to meet water quality objectives. Treatment technologies can be combined and tailored to fit different objectives.

How Should Research Be Conducted?

Any effort to better understand the opportunity to treat and utilize produced water outside oil and gas operations will be greatly advanced through not only applied research, but also strategic collaboration. Where research does occur, it will be vital that groups including academia, industry, and government collaborate to achieve the most substantive and useful results and work toward transparency in communicating and interacting with other interested stakeholders, including the public.

One limitation for studying produced water is researcher access to relevant produced water samples. Some leading institutions focused on this area of work have had success in developing partnerships to obtain a variety of samples. Research is likely to proceed much more quickly and effectively when research labs can partner with industry to expand availability of produced water samples for study. Collaborative identification of specific research goals and coordination among research groups may also help to promote such partnerships and foster the sharing of samples to further investigation of a reuse application or study.

The need for effective and informed decision-making on produced water management alternatives has also prompted collaboration among agencies responsible for oversight. As an example, the State of New Mexico and EPA Region 6 entered into a Memorandum of Understanding in 2018 to investigate the regulatory landscape for produced water reuse. The MOU involves three distinct New Mexico state agencies, as well as both Region 6 and EPA headquarters, who developed a draft white paper aimed at clarifying the permitting and regulatory regime for produced water in the State. The draft white paper became available in November 2018; as of the date of this publication a final has not been published.

FIT FOR PURPOSE

The phrase “fit for purpose” can have multiple meanings. In this module, it signals that the process, action, tool, or technology being discussed is expected to be implemented, utilized, or designed to meet targeted goals unique to the reuse scenario being considered. “Fit for purpose” commonly describes the level of treatment applied to a water in order to meet water quality objectives, as illustrated in Figure 3-5. Treatment technologies can be combined and tailored to fit different objectives.

The same tailored-approach concept is used in this module to refer to research or information gathering objectives as well as risk-management strategies. Depending on the reuse strategy proposed, the questions and considerations involved in identifying and mitigating risks will vary and will also need to be “fit for purpose.” Because produced water is highly variable and the range of potential end-use options includes many diverse factors, the “fit-for-purpose” concept is useful to reinforce the need for flexibility and adaptability in evaluating reuse scenarios.

Potential Reuse Scenarios
Several alternative disposal and potential reuse options for produced water are now active or may be considered in the future. Reuse may involve consumption or application to land or discharge to water and may occur in an agricultural, municipal, or industrial setting.

The ideas and examples provided are not exhaustive and represent a subset of reuse applications identified elsewhere, such as in the EPA guidelines for water reuse. Factors impacting feasibility of potential uses (such as logistics, cost, health or environmental risk assessment, regulations, public perception and acceptance, etc.) must be fully considered and will be discussed in later sections.

Many reuse opportunities remain at a conceptual evaluation stage. Where scientific evaluation of risk or other considerations have occurred or are underway, study has primarily been based in laboratories at bench scale or in a limited pilot scale. Field studies are typically costlier and currently less common but can provide real-world data that can confirm opportunities or reveal practical challenges for full-scale implementation.

Reuse options that are active or being tested tend to be in response to localized factors such as:

- Availability of produced water, usually at lower-than-average salinities (and often extracted via conventional production methods or from coalbed methane wells);
- Limited, costly, or nonexistent disposal options;
- Defined need for additional water in the local area;
- Reasonable costs to transport and treat produced water relative to costs of other options for water sourcing or disposal; and
- Appropriate permitting schemes and/or associated regulatory requirements that can be met within the cost framework.

This report identifies three general categories of reuse: (1) land application, (2) water discharges, and (3) industrial uses. Consumption is also included briefly, though limited primarily to the context of livestock or wildlife. Most scenarios will demand some level of treatment and any reuse must meet all applicable regulatory and permitting requirements. Research in support of decision-making should characterize and address associated health and environmental risks.

As projects advance to full-scale application it will be important for all parties to recognize the different terminology that is used in various states or industries. While discharge to a surface water body may be considered a reuse in some circumstances, it may be considered disposal in others. Likewise, land application may be considered disposal under some conditions but in others as a beneficial use for irrigation purposes.

A summary of current literature and previous or ongoing studies on this topic is included in the “State of the Science: Literature Review” section of this module.

Land Application
Several active or potential reuse options center on land application. Produced water may reach land application end users through direct transfer or through other delivery mechanisms such as upstream surface water discharges or aquifer storage projects that increase water available for withdrawal. Most land application scenarios use produced water to replace or supplement fresh water or other brines in (1) irrigation or (2) ice or dust suppression. The levels of treatment for these purposes will vary. This section does not address other mechanisms for land-based disposal such as land farming.

Crop irrigation can range from non-food crops like cotton to food crops for human consumption such as fruit and nut trees. Treated produced water irrigation for crops like hay or livestock feed has not been widely studied but may be in the future. Irrigation could also include municipal use to water


131 In 2015, Anadarko and Energy Water solutions partnered with Texas A&M AgriLife Research on a study in Pecos, Texas to investigate irrigation of cotton with desalinated produced water blended with well water (1:4 ratio) as compared to existing well water and also evaluate soil salinity parameters. The study found that the blend did not reduce cotton yield or lint quality and may improve soil salinity as compared to the well water. https://vprcolostate.edu/few/wp-content/uploads/sites/14/2016/07/Lewis-TAMU-AGL-NSF-FEW-workshop-12-2015.pdf.
Active Land Application: Crop Irrigation. One example of crop irrigation can be found in the Cawelo Water District, near Bakersfield, California, where produced waters are uniquely low in total dissolved solids and other constituents. Produced water in this region has been treated, blended, and used for irrigation for some time. Recently, studies have been ordered to evaluate chemical exposure and health risks associated with human consumption of the irrigated fruit, vegetable and nut crops.* Regulators have also been given the authority to gather additional information by requiring reporting of all additives used or supplied to operators who operate wells that supply produced water for reuse in order to further inform analysis of the practice.** Public concerns about the use of produced water in agriculture have also prompted the Regional Water Quality Control Board to set up a Food Safety Panel consisting of academics, regulators, and consulting scientists to review the practice, assess risk, and make recommendations in a forthcoming white paper.† More information on this reuse scenario can be found later in this module.

* The California Water Board has a website dedicated to this study that gathers all relevant disclosures, reports, studies, etc. and includes a discussion of the ongoing Food Safety Panel Process. [https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/](https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/)

** The authority for the orders is California Water Code §13267.5, which became effective on January 1, 2018. The Water Board has compiled a list of oilfield additives from these reports at [https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/data/2018_0628_additive_info.pdf](https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/data/2018_0628_additive_info.pdf)


golf courses, road medians, parks, or athletic fields, though this type of use does not appear to have been investigated. The type of irrigation proposed will dictate research and regulatory needs, given that risks to health or the environment will vary depending on the expected exposure pathways and other scenario-specific considerations.

Other land application options include the use of produced water or brine derived from produced water for de-icing of roadways or dust suppression on roads or open land. Roadspreading is one current reuse example where produced water may not be required to be treated (beyond basic separation, settling, etc.) before application, though where allowed most states require some form of chemical characterization to be reported. Various states permit this use, though recent concerns from local communities, regulators, academics, and legislators have led to increased attention and investigation of its utility and potential impacts. Some road application scenarios have proceeded without issue. Pennsylvania is one area with advanced study of this application – studies there have focused on analyzing the produced water used for road application for radiological constituents of potential concern,132 and others have shown that this application method can result in accumulations of alkali-earth elements (including radium) in soils near roadways.133 There has also been some indication that produced water may actually be ineffective for dust suppression in some locations.134 Associated environmental or health risks or consequences have not been fully identified, as the study of this application scenario is ongoing.


134 Kayla Graber, Christina L.M. Hagiss, Jack E. Norland, and Thomas DeSutter, “Is Oil-Well Produced Water Effective in Abating Road Dust?,” Water, Air, & Soil Pollution 228:449 (November 2017), [https://doi.org/10.1007/s11270-017-3640-x](https://doi.org/10.1007/s11270-017-3640-x) (Graber et al. also emphasized the potential for metals to accumulate in soils near roadways where produced water was applied).
**Study or Investigation of Land Application: Crop Irrigation.** Researchers from Colorado State University and the United States Department of Agriculture (USDA) collaborated on a greenhouse study investigating the use of treated Denver-Julesburg Basin produced water for irrigation of two salt-tolerant biofuel crops, switchgrass and rapeseed. Researchers evaluated different produced waters with varying total organic carbon (TOC) and total dissolved solids (TDS) levels and relative impacts on seedling emergence, biomass yield, plant height, leaf electrolyte leakages, and plant uptake over one growing season. The research found that higher levels of both TOC and TDS had negative impacts on multiple endpoints, including yield and growth health, and concluded that organic content is potentially a greater quality constraint than salinity. The authors hypothesized that such studies and related findings could inform regulatory decision-making on treatment standards for irrigation. For example, the authors discussed potential optimum treatment levels to at least 3500 mg/L TDS to maintain yield and plant health, removal of organic matter to less than 50 mg/L in order to keep leaf cell damage to less than 50 percent, and a TOC of less than 5 mg/l to keep a “sustainable biomass production rate.”


Some states have conducted their own studies regarding the impacts and appropriate regulatory parameters for land or roadspreading of produced water in response to a number of drivers including community concern. For example, North Dakota conducted a study and implemented new guidelines for use of produced water in de-icing or dust suppression. Similarly, Colorado policymakers are in the process of deciding whether and how to allow or regulate these practices. The Colorado Department of Public Health and Environment developed a report on nationwide practices and risk-related considerations for roadspreading in response to public concern over potential health and environmental impacts. Reconsideration of roadspreading authorization and permitting provisions is also ongoing in Pennsylvania.

**REGULATORY VARIABILITY AND ROADSPREADING**

Roadspreading is an example that highlights the need for fit-for-purpose risk assessment and use-determination based on different produced water qualities and application circumstances. This variability is reflected in regulatory programs. States differ significantly on their allowance and specific regulation of roadspreading or land application for dust suppression, de-icing, or other purposes. Common regulatory variables can include land owner approval, setbacks, chemical characterization, beneficial use determinations, or limitations on the type of produced water used (e.g., conventional or unconventional; flowback fluids or formation water; TDS level). Some states through either legislation or regulation allow this practice through permitting programs or local ordinances with some specific limitations (e.g., Alaska, Ohio, West Virginia, Wyoming and others) and other states either ban or do not actively permit this use (e.g., Alabama, Idaho, Texas). Pennsylvania has recently halted authorization of this practice.

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Discharges to Water Bodies

Reuses to replenish water resources may occur through (1) discharge to surface water or (2) injection into subsurface zones. In a vast majority of cases, treatment will be needed prior to surface water discharge or aquifer injection and permitting will be required through federal, state, regional, or local authorities. Where feasibility is determined and risks are deemed acceptable and manageable, the potential benefits of new water volumes may create incentives for advanced treatment for discharge where allowed under current regulations, particularly in western states where a new water source or water rights may have significant economic value.

Whether or not the receiving body is a “Water of the United States” (WOTUS) may determine the applicable regulatory and permitting regime. State definitions of regulated water bodies is also a determining factor. Discharges to surface water can provide an alternative management option for treated produced water or serve specific intended purposes such as agriculture use and wildlife propagation (see, e.g., 40 CFR Part 435, Subpart E), allowing for produced water discharges where it has a use in agriculture or wildlife propagation when discharged). Regulatory considerations are outlined in more detail later in this module.

Another potential water reuse scenario is injection into groundwater for near-term or future use (known commonly as aquifer storage and recovery or ASR, or managed aquifer recharge). A clear example of this use has not been identified in literature reviewed for this report, though there may be interest in this option in the future with further study into treatment technologies as well as health and environmental risks, particularly as it may allow for long-term, large-volume storage of treated water. Preserving the quality of groundwater is a key objective for this reuse option.

Treated produced water has been proposed by at least one study for streamflow enhancement and ecosystem services, although treatment to suitable water quality standards would be a key consideration for this use and could be expensive. Treated produced water also could be used to prevent salt water intrusion in coastal regions or to address subsidence or compaction in oil producing regions. Two articles on such uses have been identified.

Industrial Applications

Some industrial applications may prove feasible as reuse options for produced water, which may or may not require treatment, including (1) replacement of a fresh, saline, or otherwise degraded water or feedstream for an industrial process and (2) mining, processing, or manufacturing of other products from the treatment of produced water for sale or use. Feasibility will depend on such considerations as geographic proximity, economics, and policy and regulation, as well as appropriate risk analysis. Where exposure pathways are limited, quality requirements necessary to prevent ecosystem or health impacts may be reduced in an industrial context as compared to other applications, though this proposition should be further investigated. Most examples provided below are in research phases and have not been actively applied to date.

Seawater and brackish water have been used since the 1970s in some coastal locations as once-through cooling water in power-production cooling towers. This application may be a potential reuse option for treated produced water, though further investigation regarding the impacts on the industrial process itself as well as implications for eventual discharge requirements remains necessary. Treatment of saline and CBM waters for these types of uses has been investigated in several studies. Despite the potential for corrosion and scale deposition, there may be an


Potential Industrial Applications. Researchers have presented technical and economic analyses of theoretical produced water use in cooling for the San Juan Generating station in northwestern New Mexico. Others have investigated use for boiler makeup water in industrial plants, though this application would require desalination at a minimum. Another hypothetical use of produced water is as a replacement for other water sources in Class III UIC solution mining, a process used to recover minerals from deposits. For example, potash mines in southeastern New Mexico use saline water in ore processing. Some mines also use salt water brines for solution mining. In theory, treated produced water from the nearby Permian Basin could be an alternative source of water for mine processing, although local economics, supplies, and logistics among other appropriate considerations would dictate feasibility.

Produced water containing large amounts of salts and minerals could be a useful source for extraction. Chemicals that may be extracted in economically useful quantities in theory include gypsum, sodium chloride, magnesium chloride, magnesium sulfate, bicarbonate, bromide, iodine, lithium salts, potassium salts, and metals such as copper. Generating valuable byproducts has the potential to enhance economic feasibility of advanced produced water treatment to meet water quality requirements for other produced water reuse scenarios. There is also interest in extracting rare earth elements, though practical and economic feasibility of this process has not yet been extensively demonstrated.

Produced water could also be a source of brine for chemical synthesis, including acids or alkalis (caustic soda or bases). While testing of brackish water concentrate for these purposes (similar salinities to produced water in some regions) has moved into commercial development, use of produced water itself as an industrial chemical source remains theoretical. The chemistry of produced water is much more complex and as such may prove less cost effective due to additional treatment requirements.

Use of produced water in algae cultivation for biofuels and coproduct generation has been identified as a future potential reuse. Because this option does not release produced water outside lined cultivation ponds, no discharge permit would be required.

AGRICULTURAL AND WILDLIFE USES

The reuse of treated produced water for agriculture or wildlife purposes actively occurs in some areas of the country today and is a primary consideration in many options proposed for the future. The guidelines and permitting policies regulating these uses are discussed both in Module 1 and the regulatory section immediately below.

Delivery for reuse of treated produced water in irrigation, agriculture, or for wildlife can occur via a variety of means including surface water discharge for downstream use, direct conveyance, or injection into an aquifer for later reuse. Often, produced water is used or being actively considered for these purposes where other sources of water are stressed or limited. The considerations included in this module to advance understanding of treated produced waters and identify and mitigate any potential risks from reuse for health and the environment should inform decision-making on this type of use as well as others.


143 For example, http://envirowaterminerals.com/projects.html.

Regulatory Studies, Examples, and other Permitting Considerations for Reuse

Module 1 of this report provides a substantive overview of the current regulatory environment related to produced water management, disposal, and reuse. This section highlights additional regulatory studies, potential permit provisions, water quality standards, and other considerations specific to reuse or discharge outside of oil and gas operations. The intent is not to provide an exhaustive overview of state and federal provisions that related to produced water reuse, but rather to present examples highlighting the range of ongoing or potential regulatory considerations that have or may come into play.

EPA Study and Regulation of Oil and Gas Discharges

While most governance related to water and oil and gas occurs at the state or local level, the EPA’s Clean Water Act (CWA) authority has implications for surface water discharges, namely through the National Pollutant Discharge Elimination System (NPDES) permitting program. The baseline CWA regulations that specifically apply to produced water date back to rules passed in the 1970s (e.g., effluent limitation guidelines (ELG) for the oil and gas extraction point source category, 40 CFR pt. 435 (41 Fed. Reg. 44942 (Oct 13, 1976); 44 Fed. Reg. 22069 (April 13, 1979)). However, in recent years the EPA has devoted significant time and resources into further studying both treated and untreated produced water and discharge practices and regulations – building on outcomes and findings of earlier studies to inform more active and directed investigations today. Efforts include:

- **Study of oil and gas extraction wastewater management** (2018-2019): In 2018, EPA launched an effort to engage with states, tribes, and stakeholders to consider available approaches to manage produced water at onshore facilities. EPA staff consulted with state, industry, academic, and NGO representatives across the country on a variety of issues related to produced water management and potential discharges under the NPDES program from all potential sites and facilities.¹⁴⁵ In October of 2018, EPA held a public meeting to take further comment and share the results of their study to-date.¹⁴⁶ A white paper on the effort is expected in 2019 and will inform EPA decision-making on whether to revisit the existing regulatory programs for discharge of oil and gas extraction wastewater.

- **Centralized waste treatment** (2014 – 2017; published May 2018): Discharges of treated produced water may occur through centralized waste treatment (CWT) facilities offsite from oil and gas operations under industrial effluent limitation guidelines in 40 CFR pt. 437 (65 Fed. Reg. 81300 (Dec. 22, 2000)), though EPA has indicated in the past that these standards were not written with produced water in mind.¹⁴⁷ In 2018, EPA published a study of facilities historically and currently accepting oil and gas produced waters under the CWT effluent limitation guidelines (40 CFR pt. 437).¹⁴⁸ EPA’s report provided detailed analysis in a number of areas of interest: identification of CWT facilities that accept oil and gas extraction wastes (including produced water); regulatory status and permitting of facilities; characteristics of wastewaters; applicable treatment technologies and their costs and performance; economic and financial characteristics of the CWT industry; documented and potential human health and environmental impacts of discharges; and generation and management of treatment residuals and transfer of pollutants to other media (like solid wastes and air emissions). The report demonstrated that CWTs can be a viable option for produced water treatment and discharge and that the necessary treatment technologies can be cost-competitive under certain circumstances. However, EPA also made a number

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¹⁴⁵ USEPA, Study of Oil and Gas Extraction Wastewater Management, [https://www.epa.gov/eg/study-oil-and-gas-extraction-wastewater-management#public-meeting](https://www.epa.gov/eg/study-oil-and-gas-extraction-wastewater-management#public-meeting) (last visited Oct. 21, 2018).

¹⁴⁶ EPA Presentation – Oil and Gas Study (October 9, 2018), [https://www.epa.gov/eg/oil-and-gas-extraction-wastewater-management-study-documents](https://www.epa.gov/eg/oil-and-gas-extraction-wastewater-management-study-documents).


of findings that highlighted challenges of the CWT program as applied to produced water – including treatment cost, lack of standards designed for produced water, analytical challenges, facilities with inappropriate technologies that may discharge pollutants of concern, solid waste management challenges, and recorded impacts of existing or historic discharges. The Executive Summary of EPA’s report is included in Appendix 3-A.

- **Hydraulic fracturing study** (2010 – 2015; published December 2016). In 2016, EPA finalized a broad study of potential drinking water impacts from the ‘hydraulic fracturing water cycle’ that included water-related considerations from acquisition to disposal, not just for hydraulic fracturing itself. In the report’s Executive Summary, EPA identifies activities that may result in impacts to drinking water, including the “discharge of inadequately treated hydraulic fracturing wastewater to surface water resources.” This observation reinforces the importance of ensuring adequate treatment to meet applicable water quality criteria in reuse scenarios involving discharges to surface waters that may serve as drinking water supplies.

- **Pretreatment standards for the oil and gas extraction point source category** (Final, June 28, 2016): In 2016, EPA finalized a rule that prohibits indirect discharges of produced water from unconventional oil and gas operating facilities through publicly owned treatment works, or POTWs. Recognizing some challenges related to its definition of unconventional and conventional, particularly in relation to ongoing practices in Pennsylvania, EPA extended the compliance deadline for the affected facilities with a December of 2016 amendment.

### The 98th meridian

While onshore effluent limitation guidelines generally prohibit the discharge of pollutants from oil and gas extraction facilities, there is a key exception that was written for more arid, western states. Subpart E of 40 CFR Part 435 applies to onshore facilities west of the 98th meridian for which “the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters” (40 CFR §435.50). EPA defines that phrase further to mean that “produced water is of good enough quality to be used for wildlife or livestock watering or other agricultural uses and that the produced water is actually put to such use during periods of discharge” (40 CFR §435.51(c)) and the associated effluent limitation is a 35 mg/L daily maximum for oil and grease (§435.52(b)).

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The decision on what constitutes “good enough quality” and satisfactory representation that the appropriate uses are in place to qualify for coverage under this ELG is left to the permitting authority. There is no publicly accessible compilation on the number of permits issued under this ELG or the volumes discharged. However, some states, and in some cases the appropriate EPA Region, have issued individual or general permits for discharges west of the 98th meridian.

Examples include:

• **Colorado general permit.** The Colorado Department of Public Health and Environment established a General Permit (permit No. COG-840000) for Discharges Associated with Produced Water Treatment Facilities.¹⁵² The permit takes into consideration not only the 40 CFR Part 435, Subpart E ELG, but also other Colorado regulations, and state water quality numeric and narrative standards. While some discharge and monitoring requirements are established in the permit, including a 3500 mg/L TDS 30-day average, constituents such as radium, organics, or other radionuclides, as deemed necessary, can be established on a case by case basis. The permit also establishes quarterly acute and chronic Whole Effluent Toxicity (WET) testing requirements.

• **California produced water discharge – Pismo Creek.**¹⁵³ The Arroyo Grande Produced Water Reclamation Facility produces reclaimed water via treatment of produced water from nearby oil wells. The water may include flow from above or below the hydrocarbon zone or flow from an injection recovery facility. The facility utilizes two phases of treatment. The first phase consists of warm-lime softening, microfiltration to remove particulates, strong-acid cation softening, and cooling of the produced water. Miscellaneous plant wastewater is incorporated into the waste stream before the beginning of the second phase. The second phase of treatment includes a two-pass reverse osmosis (RO) system, weak-ion exchange ammonia (NH₃) removal, chemical polishing, storage, cooling, and aeration. The treated water goes to irrigation use; while unused treated water is discharged into nearby Pismo Creek, with volumes not to exceed 0.84 million gallons per day (MGD). That discharge is regulated by a National Pollutant Discharge Elimination System (NPDES) permit, which must be renewed every five years and is subject to the technology-based effluent limitations established for discharges west of the 98th meridian under 40 C.F.R. Part 435 Subpart E.

As part of the initial permitting process, the facility owner submitted documentation that the discharge contributes to recharging groundwater used for agricultural purposes downstream. Additionally, the facility submitted documentation stating that the discharge will contribute to recharging groundwater in a manner that will help prevent and/or reduce potential seawater intrusion. The regulatory agency has concluded that discharged water quality is adequate to support wildlife in and around Pismo Creek, and monitoring and reporting requirements are included in the permit to provide monthly compliance data.

• **Wyoming application for permit to surface discharge produced water (short form C).** In September of 2018 the Wyoming Department of Environmental Protection updated its application for a permit for surface water discharges of produced water (see Appendix 3-B). In addition to basic outfall information, the application requires a description of measures to prevent access to ponds from grazing animals and birds, treatment and control measures to meet standards and prevent erosion, and a list of all potential pollutants expected to be in the discharge. Lab analysis and reports for water proposed for discharge is required for 35 parameters with required detection limits. Examples of the standards...
for discharge of certain constituents include barium (2000 ug/L), boron (5000 ug/L), chloride (2000 mg/L or 230 mg/L for higher water classes), Radium 226 (5 or 60 pCi/L), and TDS (5,000 mg/L). The permittee must also provide documentation that the produced water will be used for agriculture or wildlife during periods of discharge for each outfall in the application.

Role of state standards

Federal standards are not the only standards that are of importance in the consideration of various reuse scenarios. For example, as made clear by the 98th meridian discussion above, discharges to surface waters will also have to incorporate applicable state water quality narrative or numerical standards and any other requirements deemed necessary by the permitting authority. The interpretation of the anti-degradation provision of the water quality standards will also be important since this could preclude the addition of a contaminant even if there is no impairment. There may be a need to develop new or modified water quality standards where new or changing practices for produced water reuse or discharge are proposed or implemented. While revisiting existing standards (including those that may make certain uses impractical or impossible) may present an opportunity to expand options for produced water reuse, the development of new standards may also present challenges in some cases due to the need for expanded research, data, or analytical tools. State permits and decision-making on reuse may also consider a variety of standards, guidelines, permits, or other best practices that relate to a specific end use being considered, such as quality standards for livestock watering.

Historically, states have limited their study and regulation of produced water to more traditional management practices or spill remediation. For example, in the late 1980s, Ohio conducted a study to collect better data on trace metals in brine to better understand potential for water contamination, including from the use of brine for ice control. Some states have recently adopted new programs or regulations that specifically address reuse of produced water. Many of these aim to further recycling of produced water for reuse in oil and gas operations are discussed in Module 2. Some standards have also had implications for treatment goals at centralized facilities. For example, Pennsylvania’s WMGR123 is a general permit for the processing and beneficial use of oil and gas liquid waste to develop or hydraulically fracture an oil or gas well. Treatment to meet the standards in Appendix A of WMGR123 effectively allows for treated water to be “dewasted” by definition, and as such transported and stored under the same standards as fresh water. Some CWT facilities in Pennsylvania treat to meet this standard as well as the discharge permit standards in order to provide dewasted water to operators for reuse. The WMGR123 permit also incorporates a Pennsylvania Water Quality standard for TDS established specifically for “new and expanding treated discharges of wastewater resulting from fracturing, production, field exploration, drilling or well completion of natural gas wells.” The new water quality standard allows authorization of discharges only from CWTs or from POTWs after treatment at a CWT, and establishes monthly average limits of 500 mg/L TDS; 250 mg/L total chlorides; 10 mg/L total barium; and 10 mg/L total strontium.

Appendix A from Pennsylvania’s WMGR123 permit is included below (Table 3-1), listing the treatment standards for a set group of constituents.
Regulatory authority

Questions are likely within a state and between state and federal authorities in order to clarify the regulatory authority or authorities for a certain end use. Within a state, some agencies that may not traditionally deal with oil and gas operations may need to be consulted or advised regarding new reuse scenarios for produced water. This might include agencies such as the water quality divisions, waste divisions, departments of transportation, fish and wildlife, agriculture, or others. In addition, where regulatory authority is not already clarified in statutes, a state’s department of environmental quality (or other environmental, health, and natural resource agencies) and oil and gas agency may need to establish clear authorities for produced water reuse and/or introduction to water bodies (e.g., discharges to surface water or, injection into aquifers or infiltration to ground water). Similar clarification exercises may be appropriate between a state and the EPA, particularly where a state may not have primacy to implement certain statutes under the Clean Water Act.

An example of such an initiative is the state of New Mexico and EPA Region VI Memorandum of Understanding to clarify the regulatory structures and roles for produced water in New Mexico.\(^\text{158}\)

Finally, local authorities cannot be forgotten. Parties seeking to pursue produced water reuse projects should work to understand and build relationships with local and county governments or other local leaders and decision-makers, including landowners and other stakeholders. State and federal requirements are often the minimum that must be met, and local authorities who work to protect local interests can have significant impacts on the success of a project.

Legislative Efforts and Impacts on Reuse Decisions. Legislation can also have an impact on reuse research and practices. For example, in 2002, the New Mexico Legislature passed a limited-term bill intended to promote treatment and discharge of produced water to the Pecos River via a tax credit (HR388).* The tax credit was set at $1,000 per acre foot of treated water (about $0.13/barrel), not to exceed $400,000 per year per company. The legislature acted on this issue namely because the Pecos watershed was strongly impacted by drought in the preceding years, and additional recharge to the river was intended to support delivery of water downstream to Texas to meet water compact obligations. A consortium of water authorities in Lea and Eddy counties in southeastern New Mexico paid for studies that examined the costs, infrastructure needs, and feasibility of treating and discharging produced water.** No discharges ever occurred (likely due to the cost of treatment as compared to the credit), and the legislation has expired; however the reports remain a useful and detailed assessment of the legal, technological, and economic requirements for enabling discharge of produced water in 2004 in New Mexico.

** NRCE, Inc., Water in the Desert: Engineering/Legal/Logistical Study to Implement the Conversion of Oil and Gas Produced Water to Useable Water in Lea and Eddy Counties, New Mexico, ”Executive Summary,” (January 2004); M. F. McGovern and E. E. Smith, Delivery of Treated Produced Water from Indian Basin and Dagger Draw to the Pecos River, Eddy County, New Mexico: Concept Report and Cost Analysis, R.T. Hicks, Consultants, Ltd., (2003).

Research and Evaluation of Reuse Options: A Decision-Making Framework

Any expansion of produced water reuse or discharge outside oil and gas operations will come with a host of questions from a variety of stakeholders. These stakeholders and decision-makers range from regulators and operators to environmental groups as well as the potential end-users of treated produced water. A common question will be, “What are the benefits and risks?”

There has been rapid growth in both research and technology development aimed at characterizing and treating produced water – initially for the purpose of reuse within oil and gas operations. As attention turns toward more in-depth assessment of the potential for other alternatives, the scope of considerations expands significantly to include new, complex issues ranging from liability to potential ecological and health hazards.

As the National Research Council has noted, the “pursuit of the best scientific understanding is inevitably resource-intensive and time-intensive, and this leads to conflict with other objectives and with constraints on resources.”159 This fact underscored why a framework is needed to identify critical questions to support smart decisions, recognizing these potential conflicts while aiming to maximize potential benefits and reduce impacts to health and the environment.

Evidence-based risk assessment serves as a vital component for informed decision-making. While the desire to use treated produced water for various purposes in lieu of disposal is understandable, the regulations or guidelines currently in place to ensure that the range of potential uses can be safely achieved may be limited. Decision-makers who have the responsibility for protecting people and the environment, need to weigh potential benefits and risks. The decision-making and risk assessment process should be based on the understanding that produced water from oil and gas operations is a complex mixture with a composition that may be difficult to precisely characterize, though adequate fit-for-purpose characterization should ultimately be achievable. Sufficient understanding of constituents of concern prior to treatment will be required to design appropriate treatment.

systems and assess the efficacy of the treatment, as well as identify and define potential constituents of concern for monitoring and limitation in specific discharge or reuse scenarios. Basing an assessment only on well-known constituents of concern or by using standards that exist today for other purposes may not be sufficient. Reuse for a specific non-industrial purpose should be based on evidence showing that the actual receptors of interest (human, agricultural, ecological, and terrestrial) will not be exposed to hazards in such a way as to cause harm. As such, defining the appropriate standards for assessment and risk management will require investigation and research.

The need for water should not justify bypassing a risk assessment process. Movement toward new reuse options will likely be supported more quickly and broadly where decision-makers and risk assessors provide consistent, transparent, and scientifically robust assessments, and openly engage and communicate with stakeholders regarding their plans and findings.

This section brings together what is known and unknown to better represent the holistic challenge at hand and a potential path forward. What do stakeholders need to know about produced water to make informed decisions about its treatment and use in potential reuse scenarios? What can be done to better identify and reduce risks to the environment and human health? What other important trade-offs or considerations must be addressed for reuse proposals to move forward? Overall, how do we assess and manage potential and perceived risks?

**Science and Risk-Based Decision Making: General**

The incorporation of risk into decision making for the permitting of new practices is not unique to the assessment of treated produced water reuse. In fact, numerous books, guidelines, rules, and policies have been written promoting the use of risk-based science in decision-making. As research and collaborative efforts progress to investigate opportunities to reuse treated produced water, past experience and available materials should be referenced and leveraged, if applicable.

One example resource is the book *Science and Decisions: Advancing Risk Assessment*, published by the National Research Council (NRC). The NRC provides a substantive discussion of the fundamentals involved in assessing risk and utilizing research and information to support decisions. The book includes a variety of iterations on the process, including the general framework shown in Figure 3-8:

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**Who Are the ‘Decision Makers’?** A number of stakeholders may be involved or should be considered in evaluating new management practices for produced water. Some of these may not be obvious “decision makers,” but their unique perception of the issues and influence on a path forward may be significant. Each stakeholder is likely to bring a different set of concerns and considerations to the table at different stages, and there will be different types of decisions to be made.

These stakeholders may include:

- **Operators**, who will determine whether costs and risks favor a new water management strategy
- **Regulators and legislators**, who will determine whether and how to permit and monitor new practices
- **New end users**, who will seek sufficient reliability, quality, and comfort to use a new water source
- **Communities and municipalities**, whose residents will have specific local considerations
- **Special interests**, whose members will be focused on endangered species, wildlife habitat, recreation, watershed, and groundwater protection
- **Property and mineral owners**, whose interests may be impacted
- **General public**, who will have questions about safety, health, and unknowns.

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160 Ibid.
The NRC also makes salient points about the process and benefits of risk assessment. Some important concepts discussed are the benefits of and value obtained from the risk assessment process. NRC notes:

“Given the demands of health and environmental decision-making, perhaps the most appropriate element of quality in risk-assessment products is captured in their ability to improve the capacity of decision-makers to make informed decisions in the presence of substantial, inevitable and irreducible uncertainty. A secondary but surely important quality is the ability of the assessment products to improve other stakeholders’ understanding and to foster and support the broader public interests in the quality of the decision-making process (for example, fairness, transparency, and efficiency). Those attributes are difficult to measure, and some elements of quality often cannot be judged until sometime after the completion of the risk assessment.”

Other groups have developed guidelines and documents related specifically to water and wastewater reuse. In a 2018 webinar on water reuse, EPA experts from the Office of Research and Development (ORD) National Exposure Research Lab reviewed key considerations by EPA and others. The ORD presented the challenge of finding new water resources with three seemingly simple questions:

1. how to define the acceptable treatment,
2. how to monitor treatment effectiveness, and
3. does it make sense to do this?

These questions present a useful parallel to the evaluation of produced water treatment and reuse.

**COMBINING RISK**

A key learning from other reuse scenarios is the need to manage the conversation regarding risk — a concept that is not unfamiliar for oil and gas operators and regulators. Risk communication must be transparent and focus on educating the public about actual risk in order to avoid fear or assumptions of unrealistic impacts. Data, transparency, communication, and expanded opportunities for information sharing can help to prevent misperceptions.

Expanding reuse practices can take time and resources. Research consortiums, multi-stakeholder groups, and other organizations are working to
understand and work toward implementation of reuse scenarios for other waters. The US Water Alliance partnered with the Water Research Foundation to establish the National Blue Ribbon Commission for Onsite Non-potable Water Systems to look for innovative solutions, allow for knowledge exchange, develop guidance and frameworks, identify research needs, and develop resources\textsuperscript{163} for onsite non-potable water systems that could be used to recycle graywater, stormwater, rainwater, etc. from buildings or other sources to replace freshwater use for things like toilet flushing, cooling, or irrigation. The Water Environment & Reuse Foundation recognized the lack of national standards or guidelines for these types of systems and developed a report that included a risk-based framework for the development of public health guidance for decentralized non-potable water systems.\textsuperscript{164} Similarly, the World Health Organization has developed guidelines on wastewater reuse in certain contexts.\textsuperscript{165} These documents describe varying approaches to assess risk, establish protective standards and best practices, advance monitoring tools, and make smart decisions that support reuse while protecting health and the environment given a range of challenges from data limitations and uncertainty to public perception.

States often conduct research and assess risk to support new programs and evaluate whether existing standards are appropriate or new standards may be necessary. For example, when Oklahoma considered Indirect Potable Reuse of domestic wastewater, the Oklahoma Water Resources Board and Oklahoma Department of Environmental Quality worked together, along with a stakeholder group including the regulated community, technical experts and the general public, to develop the new program, recognizing early in the process that the existing standards and implementation for typical point source discharges would not be adequate for the unique circumstances. After research and technical consideration, the agencies developed a program that included advanced effluent benchmarks, modeling of effluent impact to evaluate multiple factors, additional operation and maintenance requirements, and receiving water body monitoring and trend analyses. The program also involves quarterly monitoring of constituents on a list of Constituents of Emerging Concern (CEC) that requires corrective action if levels are exceeded, while also collecting data that informs the development of a more representative list of CEC’s and ongoing efforts to set risk-based screening and action levels.\textsuperscript{166} This process took about six years, with a working group convening in 2012 and new Indirect Potable Reuse rules adopted in 2018.

Water and wastewater reuse of any kind, if done incorrectly, can result in significant repercussions. Negative impacts obviously include contamination or health effects, but another risk is reluctance to try reuse again in the future. Therefore, it is vital that reuse options proceed in an informed and cautious way, particularly in early stages.

\textbf{The Framework}

The following is a general framework for the evaluation of reuse options, focusing primarily on research needs. At its foundation, the framework relies on traditional risk-assessment principles but is both modified and expanded to better address the unique challenges of produced water and recognize a broader range of important considerations. Each section is discussed in detail below the framework overview.

Assessments conducted with currently available information should recognize, where appropriate, that unknowns and uncertainties exist, and decisions should be revisited for improvements where new information, technologies, and data become available.

The framework is designed to assist decision-makers in working through analysis of a given reuse scenario, providing guidance regarding the type of questions and steps that may inform assessment of a given project. It is intended to spur discussion and

\begin{itemize}
  \item \textsuperscript{163} National Blue Ribbon Commission for Onsite Non-potable Water Systems, US Water Alliance, \url{http://uswateralliance.org/initiatives/commission}.
  \item \textsuperscript{165} See e.g., World Health Organization, \textit{Guidelines for the Safe Use of Wastewater, Excreta and Greywater – Volume 2, Wastewater use in agriculture} (2006), \url{http://www.who.int/water_sanitation_health/wastewater/wwuvol2intro.pdf}.
  \item \textsuperscript{166} Email correspondence with Oklahoma Department of Environmental Quality. See also Oklahoma DEQ Indirect Potable Reuse Rules, OAC 252:628-1-3 (adopted in 2018).
\end{itemize}
help to focus research and development efforts in a way that support decision-making on reuse in the future. While this framework seeks to serve as a useful guide in assessing a specific reuse scenario, GWPC does not intend to prescribe a single set process for assessing individual reuse proposals. Instead, GWPC expects this effort to encourage collaboration, targeted research, and further engagement surrounding this important issue, including refinement of this framework.

At present, existing data gaps in chemical and toxicological characterization of produced water present limitations for implementation of this framework for specific reuse scenarios – namely, the identification of potential constituents of concern for analysis, treatment, and monitoring. Efforts to broaden this knowledge through advancements in analytical and toxicity testing tools are ongoing and may allow for more comprehensive assessment in the future. Advancements may be furthered by pairing characterization efforts with treatment studies or pilots, where some barriers to study can be lessened through targeted treatment. Moving forward, this conceptual framework and research conducted in furtherance of this framework should be revisited as data gaps are filled by chemical disclosures, new analytical methods, treatment systems, toxicological information and the like.

The framework consists of four key phases:

• **Phase I: Preliminary review of the proposed program.** The goal of this phase is to define the scope of the proposed program and conduct an initial, cursory assessment to determine whether the reuse scenario is likely to be feasible and if additional analysis is worth investment. This may include a screening-level assessment of the known, basic chemistry of the produced water as compared to the known, basic quality needs or objectives for the end use, as well as an initial evaluation of expected treatment needs. This phase should also incorporate an initial assessment of non-research considerations such as economics, logistics, infrastructure, and public perception. Stakeholder involvement may be incorporated to better identify and address these.

• **Phase II: Identification of stressors of interest for treatment and risk analysis.** This phase is devoted to adequately characterizing the produced water and decision-making regarding appropriate treatment technologies. Characterization of both influent and treatment effluent is necessary in order to identify the “stressors” or chemicals and other constituents of interest that should be targeted for removal and further analyzed in the risk assessment phase. This phase includes both characterization and treatment technology assessment and may also incorporate research objectives on both analytical method development and treatment technology advancements and testing. The end result of this phase aims to help narrow the scope of further consideration to characterization of expected effluent and priority constituents of concern for consideration in a scenario-specific risk assessment.

• **Phase III: Risk assessment (applied to treated produced water).** Phase III focuses on a traditional risk assessment, based on models of analysis commonly employed by risk assessors and agencies. This includes hazard identification, dose-response assessment, exposure assessment, and risk characterization — all based on the proposed reuse program and expected stressor(s). While this framework focuses on the fluid itself, similar risk assessment process could be necessary for solids and other residuals from treatment, though this framework focuses on the fluid itself.

• **Phase IV: Risk management and decision making.** Phase IV aims to support an informed decision to move forward with a project and define the necessary risk management strategies. It includes a final evaluation of the considerations of Phase I, a decision on whether the risks as characterized are manageable, and an effort to implement or develop the appropriate risk management strategies, including quality standards and permit limitations, monitoring tools, best practices, and information sharing. Phase IV also recognize the importance of a process of continuous learning and incorporation of new knowledge or tools.
RISK ASSESSMENT TERMINOLOGY

- **Risk assessment**: EPA notes that risk assessment is, to the highest extent possible, a scientific process. In general terms, risk depends on three key factors: (1) how much of a chemical is present; (2) how much contact (exposure) a person or ecological receptor has; and (3) the inherent toxicity of the chemical. Risk assessments traditionally focus on individual chemicals, though assessment of complex mixtures is an increasing area of investigation.

- **Stressor**: Any physical, chemical, or biological entity that can induce an adverse response. In the context of produced water, this might be a constituent of concern or the mixture itself. Stressors may adversely affect humans, specific natural resources, entire ecosystems, or other ecological receptors.

- **Dose-Response**: Examines the relationship between an exposure and effects.

- **Exposure Assessment**: Examines what is known about the frequency, timing, and levels of contact with a stressor.

- **Hazard Identification**: Examines whether a stressor has the potential to cause harm to humans and/or ecological systems, and if so, under what circumstances.

- **Variability**: Toxic response or exposure depending upon numerous factors. Variability must be considered in risk assessment.

- **Uncertainty**: Incomplete data often means that assessors are incapable of knowing “for sure” what the risks are to people and environments. Uncertainty must be factored into account.

Figure 3-9: Framework for Research, Evaluation and Decision-Making
Phase I: Preliminary assessment of proposed program

Phase 1 Overview and Goals: The preliminary screening and assessment predicts the viability and value of a proposed reuse program. A feasibility evaluation using existing data is intended to avoid unnecessary investment of time and resources. In cases where this preliminary evaluation indicates that a reuse option may indeed be feasible, the effort expended in Phase I allows data gaps and required research to support subsequent risk characterization to be identified and scoped.

Each step of the Phase I Preliminary Assessment is detailed below.

Define proposed reuse program

Step one in this decision framework includes definition of key facts and information, such as:

- Proposed category of use: e.g., industrial, municipal, agricultural, ecological, etc.
- Identification of project drivers and expected benefits/beneficiaries
- Water volumes potentially available and needed
- Expected variability in produced water quality, quantity, availability
- Timeline and duration of project; case-specific demand considerations such as seasonality, etc.
- Location description and characterization, including potential receptors and exposure pathways
- Proposed method of delivery for reuse (e.g., discharge, pipeline, aquifer recharge)

- Available treatment technologies and projected effluent quality
- Option for management of treated water and waste streams, including solids

Desktop screening for basic feasibility

The goal is to gather readily available or obtainable information to better define known, basic water quality needs for the proposed use for comparison to the produced water that may be available or utilized. This screening step will not necessitate a thorough characterization of receptors or substantive chemical analysis of produced water. Instead, the benefit will be a basic representation of the scale of the challenge ahead. In some cases, a preliminary screening may indicate that a project is simply not currently feasible or economic. In other cases, a preliminary screening may show good promise for a potential project and support investment in further investigation.

Accelerating progress with collaboration.

Identifying producing companies and research partners willing to come together to share water, characterization, treatment, and piloting data and resources would accelerate the progress of produced water treatment and reuse.

One example is the Marcellus Shale Energy and Environment Laboratory (MSEEL), where government and academic researchers work together with industry on a long-term field site to study unconventional oil and gas development. ([www.mseel.org](http://www.mseel.org)).
The desktop analysis may involve three basic parts:

1. **Gather available guidance, standards, requirements, etc. on known water quality needs/goals for the proposed use.** The scope of this step will vary based on the intended end use. The expectation is not that the available guidance or standards will address all constituents of concern or relevance in produced water. Instead, the goal is a basic understanding of the estimated water quality objectives. Sources of information might include national water quality criteria, published literature, guidelines for water reuse, published irrigation criteria, etc.  

2. **Conduct a screening level analysis of the produced water that may be considered for a treatment and reuse program.** This step will involve analysis of known produced water constituents that are likely to be relevant to an assessment of feasibility utilizing existing, approved analytical methods. It may be possible to use existing knowledge and data or reports available on the produced water to limit this step to a desktop study. Additional resources may include MSDS data sheets and known additives utilized in operations as well as the website for hydraulic fracturing chemical disclosure, FracFocus.org. Parameters may include:
   - Basic water quality: TDS, TSS, BOD, pH, alkalinity
   - Inorganics/metal: NH3, H2S, PO4, Pb, Fe, Zn
   - Organics: TOC, TPH, BTEX, PAH, VOC, SVOC
   - Radionuclides
   - Other constituents expected to be present, based on generator knowledge and/or those common to produced water, that may pose a challenge to meeting water quality needs – for example, biocides or methanol in cold-weather locations.

3. **Preliminary assessment, treatability, and comparison to known water quality goals.** Based on available information on water quality objectives and chemical character of produced water, this step seeks to develop a basic understanding of the challenge. For example, is it economically feasible to reduce TDS to levels identified utilizing available technologies? Consider available treatment technologies needed to achieve known treatment goals and management of waste streams.

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**Initial evaluation of practical considerations**

Any decision on produced water reuse will entail practical considerations beyond those addressed explicitly in this framework. Such considerations may hold an equal or greater influence on decisions when compared to ecological or health risk concerns and, alone or collectively, can be a deciding factor for an alternative use proposal. See pages 154–161 for a more substantive overview of these considerations, which include law and regulation, public perception, logistics, economics, environment, and benefits.

**Decision: Does the preliminary assessment suggest a feasible program?**

This decision point presents an opportunity to determine if analysis conducted up until this point supports a decision to move forward with a more substantive risk characterization process or better supports the consideration of an alternative approach. Ideally, minimal effort and money have been invested in a preliminary “go/no go” decision.

“**No**” a finding that the project is not expected to be currently feasible based on a screening assessment, will lead to a consideration for alternative approaches. Such alternatives may include utilization of existing disposal methods, or alternative strategies that may lead to a use scenario after preliminary assessment and results in a “yes” decision to move forward.

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“Yes” a finding that the project may be feasible based on a screening assessment, will lead the decision-maker into a more substantive data collection and risk assessment phase.

**Phase II: Identify stressors of interest (constituents of concern) for risk assessment**

**Phase II Overview and Goals:** Better understanding the quality of produced water, including its chemical constituents, is a key need for both risk assessment and designing and testing appropriate treatment options. This phase connects a more in-depth analysis of the produced water quality proposed for reuse with research and development or identification of a fit-for-purpose treatment train, potentially including pilot testing. As much clarity, where feasible, on the constituents present in untreated produced water is useful to assess treatment efficacies and will inform which constituents should be prioritized for permitting or monitoring purposes. Phase II does not intend to imply that exhaustive characterization of produced water is a necessary requirement to move to Phase III. Instead, this phase aims to emphasize that partnering advancements in characterization with treatment technology design and assessment allows for a more informed risk assessment and management phase. This allows for the targeting of specific constituents of concern for removal, but also allows for an improved understanding of the chemicals or classes of chemicals that may be expected in liquid effluents or in solids or residuals. Importantly, initial characterization of produced water in the context of a fit-for-purpose reuse project affords an opportunity to create a more effective, robust, and protective treatment and monitoring program.

This phase represents the realities of an iterative assessment process. For example, there may be ongoing analysis necessary to identify potential stressors of concern, particularly if new or modified analytical methods are deemed necessary or become available. This means that new information may feed into the analysis in an ongoing manner, and potentially inform treatment technology design and assessment as well as effluent characteristics. The same may be true for treatment technologies, as new options are developed and tested to address various stressors or reach quality goals. Overall, it is not expected that there will be a “final” answer at this stage, but rather a recognition
of what is known and unknown, and a commitment to iterative incorporation of new data or technologies as they are developed. This process allows for continuous learning and advancement that can create more efficient and protective treatment and reuse programs. The acknowledgement of the need for such iteration, however, does not necessarily mean that a potential project should not be further analyzed or pursued given tools and knowledge available today. Finding a balance between supporting the advancement of produced water reuse projects while recognizing opportunities for knowledge and process improvement will be a key challenge.

**Decision: Adequate tools to identify/quantify potential stressors of concern?**

The aim of this decision point is to determine whether the appropriate methods exist to identify potential stressors of concern at appropriate quantification levels in the produced water for its proposed reuse. Potential stressors in produced water can be grossly broken down into general water chemistry parameters (pH, total dissolved solids, temperature, etc.), inorganic constituents (ions and metals), radionuclides, and organic chemicals. The availability of methods to quantify these four classes of constituents vary, particularly for organic constituents, which are not well characterized in produced waters. While existing methodologies are likely to exist that can greatly inform the characterization effort, there may be a need for expanded research to modify or develop new methods. Challenges associated with accuracy, interference, and other limitations associated with raw produced water are lessened significantly in treated water, but the challenges associated with a lack of methods for some constituents of concern applies regardless of the level of treatment. A key objective is ensuring that the right constituents are being removed to protective levels, and this involves an improved understanding of treatment targets. In all cases, advancing our ability to characterize the constituents of concern in produced water better equips researchers, technology developers, operators, and regulators alike with the tools and information necessary to design and assess treatment methods, carefully select indicator compounds for monitoring, or establish the appropriate limits for constituents of concern as treated produced water is considered for a new reuse option.

Existing methods can be generally described as follows:

- **General water chemistry analytical methods** include pH, total dissolved solids, alkalinity, hardness, and others that are routinely measured in water, wastewater, and produced water. These methods are established and frequently used in produced water analysis. However, interferences still exist for several of these analyses as applied to produced water. For example, turbidity interferes in USEPA Method 310.2, which measures alkalinity. As such, considerations should be taken for each method and the complexity of produced water being characterized.

- **Inorganic constituents (ions and metals) and radionuclides**, have established methods that can be used for produced waters. For example, USEPA methods 300.0 (major anions), 200.7 (metals), 901.1 (gamma emitters), and 9310 (gross alpha/beta) are certified methods that are routinely used for regulated constituents in water and wastewater (e.g., those that have Minimum Contaminant Levels [MCL]). However, the complex matrix of produced water can present challenges for these methods that were developed for fresh water. In particular, EPA method 903.0, which effectively measures isotopic radium levels in fresh water, has been demonstrated by one study to be inaccurate when applied to produced waters.

- **Some established methods for organic constituents** can be applied to produced water. For example, USEPA methods 8260 (volatile organic compounds) and 8270 (semi-volatile organic compounds) as well as USEPA methods 624 and 625 for the same constituents are...
there is a demonstrated need to develop operations learnings from existing or ongoing studies. This work may take into consideration tools (e.g., bioassays) that can quantify known or potential stressors using analytical tools or bioanalytical methods. The focus of this research objective is more informed decision-making on stressor identification. The goal of this task is to develop appropriate analytical methods or tools to more thoroughly identify and treatability of TOC.

Waters can contain total organic carbon (TOC) levels greater than 1500 mg/L (Rosenblum), with little of this TOC characterized given the lack of validated methods for quantification. As such, a likely research need is better determining the nature, toxicity and treatability of TOC.

Research Task: Modify, develop, apply additional tools/methods

The goal of this task is to develop appropriate analytical methods or tools to more thoroughly identify and quantify stressors. This research task aims to address any analytical limitations that have been identified in the decision point above and provide feedback that results in more informed decision-making on stressor identification. The focus of this research objective would include defining the path towards identifying potential stressors using analytical tools or bioanalytical tools (e.g., bioassays) that can quantify known or unknown stressors. This work may take into consideration learnings from existing or ongoing studies on this topic (see “State of the Science: Literature Review”).

Effectively applying existing methods and potentially developing new analytical tools for stressor identification is a critical step in understanding produced waters and their constituents. Robust chemical characterization begins with proper sample collection and ends with validating methods that are able to accurately quantify stressors in produced water. As previously highlighted, while many of the standard methods for waters and wastewaters that are available can be applied to produced water, some limitations that have been identified in produced water lack approved analytical methods. As a result, there may be a need to develop and gain approval of methods for constituents identified as a priority.

In one study, Oetjen et al. developed a table (Appendix 3-C) of suggested analytical methods for analyzing target analytes, based on chemical groups or types, which are likely present in produced water. Researchers developed a table that listed available methods (either research or standardized) and included any pre-treatment requirements that might be necessary. However, the research team notes that quantification of analytes in produced water will be challenging; furthermore, a combined effort of non-targeted screening to identify unknown constituents will need to be coupled with targeted analysis and method development.

Examples of research include:

- **Standard methods development and validation.** There is a demonstrated need to develop standard sampling procedures for produced water, followed by analytical method validation.

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to create standard procedures that will ensure uniform chemical characterization from lab-to-lab. This is likely to include a need for research or reference materials to validate findings and results.\(^{174}\) Method validation can be a lengthy process that requires inter-lab coordination to assure method performance meets a particular need as applied (i.e., measuring constituents at relevant concentrations).\(^{175}\) Given the time and cost associated with method development and validation, and the many potential constituents present in produced water, prioritization is challenging. Therefore, one area for initial effort is the identification of chemicals that should be prioritized for method development based on data points such as known hazards, identified presence in produced water, and expected concentrations.

- **Sample preparation and matrix interference analysis.** Numerous analyses require sample clean-up due to the complex nature of produced water and assessment is needed to confirm best practices. A common method used by analytical chemists to manage matrix interference is to simply dilute samples prior to analysis; however, for trace elements or constituents of concern that are harmful at low concentrations, this practice may detrimentally affect analytical accuracy by raising detection limits.\(^{176}\) Such assessments will validate extraction and clean-up procedures, identify key inhibitors (e.g., chloride) that can impact analysis, and demonstrate best practices on how to remove them.

- **Identification of treatment-resistant unknowns.** Potential knowledge limitations on constituents of concern that are in produced water influent streams or how those chemicals may be transformed during treatment in specific scenarios may make measuring treatment efficiency challenging. Therefore, there may be a need to identify unknowns in treatment effluents using non-targeted analytical techniques including high-resolution mass spectrometry (HRMS). It should be noted that HRMS, while able to provide valuable insight into chemical characteristics of a sample, can be time- and resource-intensive. Therefore, HRMS should be viewed as a valuable tool for research and development to identify potential constituents of concern in untreated samples.


produced water and to confirm removal during and after treatment technologies as they are tested and piloted. Subsequent monitoring and treatment assessment can be performed using less-demanding analytical techniques for priority constituents of concern found above de minimus concentrations that are likely to be treatment-resistant, are identified as being harmful at low concentrations, or on their carefully selected indicator compounds, as long as appropriate methods exist or are developed. Furthermore, while this approach can help identify unknown constituents this method does not address the collective risk posed by the combined known and unknown contaminants identified. Thus, a practical solution is to integrate whole effluent toxicity (e.g., WET assessment) or other bioanalytical tools. This is a common strategy applied in practice to other wastewater streams, such as municipal effluents, for quantifying potential effects of multiple stressors.

**Validation of toxicity bioassays.** Outside initial characterization studies or research applications, comprehensive, in-depth chemical characterization of produced water is often cost-prohibitive and may be unnecessary. However, it will be necessary to have a reliable assessment of the potential toxicity of the treated produced water proposed for reuse or discharge. Therefore, toxicity screening bioassays, which may quantify or predict the effect of both known and unknown stressors in the mixture itself, are a logical compliment to chemical characterization methods. For surface water discharges, a variety of standard WET methods are available. In the case of other reuse scenarios, such as those where land application is considered, new tests or bioassays may need to be developed and validated. Screening assays can help to identify the appropriate bioassays for risk assessment and are further discussed in the next section.

### Decision: Is proposed treatment scheme expected to reduce/remove stressors of concern?

The aim of this step is to determine whether the treatment scheme is expected to reduce or remove the constituents of concern, or stressors, in the produced water. If stressors can be identified, chemical and physical data, where available, can be used to assess which treatment technology/technologies would likely reduce these stressors. Literature or water treatment models could be used to predict treatment efficacy, however pilot- or full-scale plant data from a similar system may best describe treatment feasibility and should be used if available. To date, limited research targets the full range of specific constituents present in produced water and resulting removal through a treatment train at a full-scale level. While data may exist on removal capabilities of known treatment processes for certain classes of chemicals in other contexts, the chemistry of produced water treatment can be significantly different and therefore may often need to be tested further.

Treatment technologies are discussed at length later in this module and in a table thoroughly assessing available technologies (Appendix 3-E). Developing an appropriate treatment train is a function of understanding the removal capabilities of each technology with respect to defined stressors, specifically those that may pose particular challenges. These may include:

- General water chemistry parameters: high TDS (i.e., greater than sea water) can be difficult/costly to reduce and can limit available technology options; as can ammonia, sulfur, boron, etc.
- Inorganic constituents: heavy metals, which can impact waste character
- Organic constituents: volatile, semi-volatile, and non-volatile organic compounds, some of which may require reduction to trace levels
- Radiological constituents: constituents may co-precipitate and pose challenges for residual waste management

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177 See, e.g., USEPA, Whole effluent toxicity methods, [https://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods](https://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods).
The treatment technologies can be assessed using a variety of strategies, including:

- Literature review or desk-top modeling can be used to assess expected constituent removal, including the identification of pre-treatment systems that can increase efficiency of later treatment stages
- Laboratory and bench-scale analysis, potentially including validation with non-targeted analysis and/or bioassays
- Small-scale field pilots
- Full-scale field testing under real-time conditions

All assessment strategies will not necessarily occur during this phase. Instead, this analysis phase will likely focus on desk-top modeling and/or bench-scale testing. If these assessments indicate that there are constituents of concern that the proposed treatment system is not capable of removing, further research may be necessary.

Pilot projects for treatment technologies may serve a useful role in identifying and prioritizing constituents of concern and choosing or designing an appropriate treatment scheme and authorization program. A combination of approaches, like utilizing pilot projects, may be necessary to determine the efficiency of treatment as noted in the risk matrix previously discussed. Pilot projects can help further what might otherwise be complex and costly analysis such as identifying constituents of concern. For example, many of the analytical methods currently available were developed for the analysis of low levels of contaminants in freshwater. Though advanced characterization of untreated produced water is ideal, due to the high concentration of salts and other potential masking components, it may be necessary to utilize existing methods to approximate contaminant levels (or classes of contaminants) in produced water for fit for purpose treatment options. A pilot treatment system could yield treated water which could much more easily use existing and high-resolution methods could be more easily used for more comprehensive characterization. Pilot project data and associated characterization efforts could then be useful to inform an assessment of risk and definition of water quality and reuse objectives. The results could be used iteratively to adjust the treatment technology to provide a final treated water of acceptable quality, while also informing any necessary permitting or authorization processes.

**Research Task: Select, develop or refine technologies**

Selection or development of an effective treatment system is predicated on the assumption of a well-characterized influent stream with defined treatment goals. Once those prerequisites have been met, treatment selection, design and validation can be completed. Where established treatment processes are considered, they must be assessed for efficacies in treating produced water. Treatment technology development, improvement, and iteration can provide an ongoing feedback into treatment schemes used for various reuse scenarios. As more is learned about the stressors of concern, related risks, as well as potential regulatory requirements and considerations initially proposed technologies may need to be revisited or modified.

- Consider alternative treatment strategies capable of removing stressors
  - Alternative uses of Mature technologies
  - Emerging Technologies
  - Research on New Treatment Technologies
- Conduct treatability studies for specific stressors
  - Bench-scale testing to demonstrate stressor(s) removal (some mature technologies can be severely impacted by produced water constituents, so the need to bench-test may be an important consideration, prior to pilot)

Advancements in treatment technologies are likely to be vital to spur produced water reuse, including new technologies or technology combinations, as well as cost reductions in technology applications that are currently prohibitively expensive.

**Research: Pilot testing and effluent characterization**

The ability to test treatment trains at pilot-scale to remove constituents of concern from produced water is a critical step in validating a system. This step allows the “risk assessor” to predict chemical concentrations that will be present after treatment and potentially in waste streams. Having this information may
allow for an accurate risk assessment. In addition to understanding the efficacy of constituent removal, the objectives of pilot testing also include:

1. Evaluate process performance;
2. Quantify chemical and energy requirements;
3. Identify quantity and character of created waste stream and management plan;
4. Document treated water quality;
5. Assess (short-term) system operability and maintainability; and
6. Develop key design criteria and operating parameters for use in sizing and costing full-scale treatment facilities.

The conclusion of Phase II is expected to result in a more complete understanding of the treatment train and known character of stressors of concern that are being removed into waste streams or that may be expected in the treated water that is intended for reuse (or potentially present in the event of a treatment upset). This is a significant objective and may take noteworthy time and resources to complete. Successful efforts in these iterative research phases, however, will inform risk assessment and management frameworks, and help to prioritize investment in method and technology development, resulting in more efficient efforts to move toward approval and implementation of a specific reuse scenario.

### The Salt Challenge

Produced water is a complex waste stream that is often high in total dissolved solids (TDS). From characterization to treatment to solids management, TDS can create inherent challenges that may impact decision-making on how a produced water is reused or otherwise managed. Some of these challenges may be lessened after advanced treatment. Challenges can include:

- **Characterization:** Salt content can interfere with analytical methods by enhancing or suppressing the instrument signal or by interfering with other constituents in produced water (matrix interferences), which can lead to biased results.

- **Toxicity assessment:** The presence of moderate to high TDS can mask hazards associated with other, lower concentration constituents. Toxicity tests after treatment should consider residual risks from organic and inorganic compounds, including interactions between constituents (including remaining ions) that may not be well understood. This underscores the need to evaluate whole effluent effects alongside individual constituents. Investigation of toxicity assessment options that are less sensitive to salinity or help to address non-TDS related residual toxicity concerns may be an area of further research need.

- **Risk assessments:** Many risk assessment protocols are oriented toward potential impacts to fresh or marine systems. While many reuse scenarios will involve TDS removal, salts may remain at some level and understanding potential health and environmental impact cannot be overlooked. Low concentration constituents other than TDS that might drive residual risk and may not be identified correctly or might be underestimated. As such, the impact of any TDS and its interaction with other remaining constituents in the treated produced water proposed for reuse should be considered in risk assessment and management strategies.

- **Treatment:** TDS levels can have a significant role on the selection, design, and cost of treatment systems to meet quality objectives.

- **Residuals:** Treatment to remove TDS will result in residual concentrated brines, sludges, or solids, sometimes at very large volumes, depending upon the mechanism utilized. Planning for the management, sale, reuse, or disposal of these residuals is a significant aspect of a reuse project.
Advanced produced water treatment scenarios to meet quality objectives are likely to result in solids and other residual wastes that will require assessment and appropriate management. Assessment of the character, volume, and management strategies of these residuals for further reuse or disposal will be important not only for the entity proposing a treatment strategy, but also for the regulatory entity considering permitting requirements. Some of the considerations that regulators may take into account related to treatment residuals include:

- Depending on the treatment methodology selected, treatment of produced water can result in solid, semi-solid, and liquid residuals, including both wastes and potentially useable products.
- Because of high TDS content and large volumes of produced water, there could be large amounts of these residuals that would need to be managed if treatment of produced water becomes widespread.
- States need to consider the infrastructure needed to manage the treatment residuals.
- The management of treatment residuals may include a combination of temporary storage, surface disposal, underground disposal, and use as a product.
- The content and character of treatment residuals need to be understood in order to evaluate appropriate disposal and/or reuse.
- Regulatory status and ownership of residuals may need to be clarified in some cases. Also, the regulatory status and ownership of any reclaimed products from the treatment residuals would need to be determined.

A note on solids: One potential consideration to mitigate challenges associated with solids management is to design treatment systems that avoid crystallization or the creation of large volumes of solids. For example, designing a system to result in a concentrated brine that could be disposed in an underground injection well. The type and volume of waste expected and considerations for its management, including costs, will play a key factor in decision-making for treatment technologies.
Phase III: Risk assessment – treated produced water

Phase III Overview and Goals: The next phase of this framework moves on from the initial screening assessment and characterization of produced water, pre- and post-treatment, to a more quantitative, site-specific evaluation to aid in the final decision on the acceptability of risk and a decision whether to proceed with the proposed reuse of the produced water as treated. It resembles the EPA framework for risk assessment but is adapted to meet challenges specific to produced water.

The summary of risk assessment included here is to inform the reader of the scope of such a process. This review is not intended to be an exhaustive instructional document, but to bring awareness to the key elements of undertaking a risk assessment.

The EPA Risk Characterization Handbook defines the four key steps for human health risk assessment. For each step, the relevant and scientifically reliable information is evaluated and the related uncertainties are described:

a. Exposure Assessment – determination of the extent of human exposure to the stressor;
b. Hazard Identification – determination of whether a particular stressor (e.g., chemical, or mixture of chemicals) is or is not causally linked to particular adverse health effects, typically determined through toxicity assays;
c. Dose- or Concentration-Response Assessment – determination of the relation between the magnitude of exposure and the probability of occurrence and extent of the health effects in question; and
d. Risk Characterization – overall description of the nature and magnitude of health risk due to the stressor(s) under review.

EPA also developed guidelines specific for ecological risk assessment (USEPA 1998) calling for:

a. Problem Formulation – the evaluation of goals, selection of assessment endpoints, preparation of the conceptual model, and development of an analysis plan;
b. Analysis – the evaluation of exposure to stressors and identification of the relationship between stressor levels and effects on ecological receptors; and

While problem formulation is not a defined step in the human health assessment process, it is included in the initial planning and scoping of the work. And for this produced water framework, problem formulation is included in Phases 1 and 2, described previously.

Human and ecological risk assessments can be complex processes and typically require specific expertise to be adequately done. EPA and the National Academies of Science have developed numerous guidance documents that strive to stay current with the development of new science. Their guidance helps to ensure that the work is done in a manner that is transparent, consistent and scientifically robust.

Because this framework includes the design of a treatment system as a key pre-step, this Phase 3 process is considered to be a “residual risk assessment,” meaning that it will only assess the risk of stressors that are expected to remain in the water following the planned treatment, or those that may be present in the event of a treatment upset or error. If unacceptable risk is identified in this phase, then additional treatment may be required. Phase 4 will account for that outcome.

178 USEPA, Risk Characterization Handbook; EPA 100-B-00-002, (December 2000).
Key research steps in a risk assessment are briefly described below.

**Research Task: Exposure assessment**

The first step of the risk assessment in the Evaluation Framework is a study to identify and characterize the receptors that are likely to be exposed to the stressors in the treated produced water, and to describe the likely exposure pathway(s). In this context of exposure to produced water the term “receptor” refers to living organisms and the environment that supports them. Potential receptors could include humans, livestock, aquatic and terrestrial life, agricultural crops and the soil, groundwater and surface water necessary to support them. The identification of relevant receptors is generally aided by location-specific factors such as regulations, policy, guidelines, and stakeholder interests; for example, from state and regional agencies, agricultural organizations, and local communities. This step of identifying receptors may be done earlier, during the preliminary screening, but if so, the findings should be confirmed at this stage and updated with in-depth chemical characterization data.

Exposure conditions can vary significantly over time for any particular location. Risk assessors and risk managers will need to decide on the full reasonable range for each key exposure variable (e.g., river flow, quantity of produced water provided) to ensure that characterization appropriately covers the range of potential risks.

Exposure pathways describe how stressors reach the receptors. An exposure pathway includes five key elements:

1. **Source** – how the stressor(s) enter the environment; this includes the spatial and temporal distribution of stressor release and subsequent transport from the source
2. **Media** – describes the location to which the stressor moves
3. **Exposure** – where receptors contact the media
4. **Route** – how the stressor(s) enter the receptor, i.e., via inhalation, ingestion, dermal
5. **Receptor** – what organisms are present to be potentially exposed

All elements must be present for an exposure pathway to be complete, otherwise, a pathway is incomplete and there is no risk.

**Research recommendation:** A site-specific conceptual model is recommended to organize and communicate the linkages between stressor exposures-receptor linkages for the intended produced water reuse scenario. In developing such models, it is important to consider specific exposure pathways of concern, such as the degree to which a substance may bio-accumulate in the food chain since this will dictate the relative importance of potential dietary routes of exposure particularly to humans and higher trophic wildlife.

For example, Hagstrom et al. created a theoretical conceptual model for identifying potential exposure pathways for agricultural and livestock watering reuse utilizing produced water (Figure 3-10).

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Once the exposure pathway(s), relevant receptors, and stressors are identified, the next major step is to holistically characterize and assess exposure. This involves describing the contact between a receptor and a stressor over time, characterized by the magnitude or intensity (i.e., concentration), frequency (i.e., single, intermittent to continuous), and duration of the interaction (e.g., hours to years). The existence of relevant local receptors indicates the potential for exposure to stressors of concern in produced water, but it does not mean that a receptor is necessarily adversely affected. For adverse effects to occur, a chemical stressor or mixture of stressors has to contact the receptor long enough and at a sufficient intensity to cause the effect. Furthermore, the effect may vary from short to long term, and mild (e.g., reversible change) to severe (e.g., death, reproductive harm). Consideration must also be given to synergistic or additive effects.

Without a clear understanding of the potential for exposure decision-makers will have a difficult task defining the actual risk to the receptors. In many cases much of the information needed to assess exposure will be available from Phase II but it may require expertise to apply it to the situation being considered. In other cases, additional data collection may be needed to adequately define the exposure.

Examples of where research may be needed with respect to produced water may include:

- Defining the persistence, fate, and transport of poorly characterized chemicals in the environment, including abiotic and biotic degradation processes;\(^{181}\)
- Determining if a chemical bioaccumulates in the receptor over time; e.g., livestock, their feed, or edible crops; and
- Holistically evaluating the capacity and resilience of local systems (i.e., soils) during or after exposure to the treated produced water.

Danforth et al. identified additional considerations when evaluating long term risks from land application of produced water.\(^{182}\)

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Hazard identification is the scientific process of determining whether exposure to a stressor can cause specific adverse effects. Understanding the potential hazards of constituents that may be in the produced water treated for reuse helps to identify priority concerns. While this process can be a complex, time- and resource-intensive activity, depending on the stressor(s), receptor(s) and adverse outcome(s) being evaluated, risk assessment is predicated on understanding the hazard of potential exposure. Human or animal exposure to a stressor may generate a range of adverse effects, from mild discomfort to organ dysfunction (e.g., kidney, liver), formation of tumors, reproductive impacts, and death, among other effects. Ecosystem impacts can range from reduced biomass or growth of plants to physical or chemical alteration of habitat that reduces or eliminates its capacity to support life.

Regarding hazard identification specific to human health — sources of data may include controlled studies on humans or statistical (epidemiological) studies of human populations to examine whether there is a link between exposure to a stressor and an adverse human health effect. However, these studies of human exposures are rare. Much more common are findings from animal studies (e.g., rodents) where the animals serve as surrogates for humans or other animals that may be exposed (e.g., livestock). These studies range from quick inexpensive screening assays, e.g., in vitro assays (cellular, sub-cellular) to costlier, longer in vivo (whole animal) assays. In vitro methods can provide useful, but limited information on produced water toxicity, while in vivo approaches are needed for evaluating complex endpoints that are difficult to assess without whole animal testing. Furthermore, with the rapid advancements in biomolecular science, scientists are increasingly developing test systems consisting of human cells and computer-based models to determine and, ideally reliably predict, adverse effects of chemicals. This move away from experimental animal studies to more advanced, in-vitro human-based assays will continue and will transform how chemical toxicity testing is done. Examples of ongoing initiatives include the EPA's ToxCast™ program and interagency Tox21 programs.

Different methods are used to study the impacts on ecological receptors. As with human health risk assessment, the methods are numerous, diverse and many are scientifically complex, necessitating expert guidance to credibly complete an ecological assessment. Examples of factors that are often examined include the following:

- What level of the ecosystem is being studied?
  - Individual
  - General population
  - Life stages such as juveniles or adults
  - Different species

- What does the organism do with the stressor (e.g., excrete or accumulate) and how is this impacted by factors such as life-stage, species differences, etc.?

- What are the adverse effects; e.g., changes in reproductive rates, tumors, effects on the nervous system, and mortality?

- How long does it take for a stressor to cause an adverse effect?
  - Acute – right away or within a few hours to a day
  - Subchronic – weeks or months
  - Chronic – a significant part of a lifetime

While human health assessments focus on the potential risks to individuals, ecological assessments most often focus on potential risks to population (e.g., survival, growth) or community (species abundance or diversity) endpoints. The focus and goal of any assessment should be discussed and decided before testing begins.

The hazard identification process for all receptors begins by examining the available scientific data. If there is insufficient or conflicting existing data, then

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new toxicity studies may need to be conducted. Rapid screening level analyses are often employed initially. This task may include review of chemical hazard reports, in vitro assays, and models that predict adverse effects based on chemical structure (Structure Activity Relationship). More advanced screening for aquatic ecosystems rely on Whole Effluent Toxicity and Toxicity Identification Evaluation.

- **Whole Effluent Toxicity (WET).**\(^{185}\) WET describes the aggregate toxic effect of whole effluent exposure as measured by an organism’s response (e.g., lethality, impaired growth, or reproduction). WET tests are meant to replicate the overall effect on aquatic life from exposure to the mixture of stressors present in the effluent without requiring the identification of the specific pollutants. WET testing is a key component to implementing water quality standards under the NPDES permits program in accordance with the Clean Water Act, Section 402. WET limits are often included in permits to ensure that applicable national or state water quality criteria for aquatic life protection are met. WET test methods include two basic types; acute and chronic. EPA recommends running tests using an invertebrate and vertebrate animal, and a plant to identify the most sensitive species for use with the NPDES permits program. *Ceriodaphnia dubia* (freshwater flea) and *Pimephales promelas* (fathead minnow) are examples of EPA approved test species that serve as surrogates used in the achieving protection goals for freshwater aquatic communities. It is also important to note that states may have their own whole effluent testing processes or identified test organisms.

- **Toxicity Identification Evaluation.**\(^{186}\) Another more intensive, informative approach that aids in the evaluation of the toxicity of a water sample is Toxicity Identification Evaluation (TIE). The TIE approach is divided into phases. Phase I contains methods to characterize the physical/chemical nature of the constituents which cause toxicity. Such characteristics as solubility, volatility, partition affinity to different sorbents, and filterability are determined without specifically identifying the toxicants. Phase I results are intended as an initial step in specifically identifying the toxicants, but the data generated can also be used to identify treatment methods to remove toxicity without specific identification of the toxicants. Phase II describes methods to specifically identify toxic contaminants, such as non-polar organics, ammonia, or metals. Regulatory agencies typically require in the discharge permit further investigation when there is a WET test failure; if based on accelerated monitoring toxicity persists, a toxicity reduction evaluation may be required that includes a TIE to identify the cause(s) of toxicity. A TIE-type process may also be useful in a research-focused context to assist in identifying constituents of concern after utilizing a whole effluent toxicity test.

**Applying these concepts to produced water.** The objective in this framework is to develop sufficient evidence to support objective quality criteria for risk characterization for the receptor/stressors of interest. Current tools may not allow for the identification and determination of the toxicity of all constituents in the produced water. Rather, one or some combination of the following approaches can be used, depending on the specific needs as determined by the decision-makers.

- Identify the hazard for key constituents of concern at the maximum potential concentration that is expected for the receptor(s) of interest.

- Conduct toxicity tests on the treated produced water to assess potential for effects at levels of exposure (i.e., for discharge to surface water scenarios, following treatment and expected dilution in the receiving water) expected for the relevant receptors.

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185 USEPA, Whole Effluent Toxicity (WET), [https://www.epa.gov/npdes/whole-effluent-toxicity-wet](https://www.epa.gov/npdes/whole-effluent-toxicity-wet) (last visited February 24, 2019).

Distillation Treatments and Toxicity. Advanced treatment technologies that drastically reduce total dissolved solids (such as reverse osmosis, thermal distillation, etc.) are effective in removing many constituents of concern but can create additional challenges. For example, removing mineral content can create a water that may pose challenges ranging from corrosion to soil impacts and negative animal health consequences. The lack of minerals can lead to a failure of toxicity tests, such as the WET test because an effluent may be toxic due to the absence of salts or ions required to support aquatic life (i.e., ion imbalance toxicity). Therefore, in some cases, remineralization of the distillate or treated water may be necessary to conduct a WET test or meet other analytical or permitting requirements. See, for example, the modification for low ionic content effluents in Appendix E of CRSD Standard One (given in Appendix 3-D of this report).

Dose- or concentration-response assessments are structured experiments that define the change in adverse response in receptors as the exposure increases. These studies help to determine the “margin of safety” (MOS), which is the ratio of the lowest stressor exposure level that will produce an adverse effect in a receptor (i.e., reference dose) to the predicted highest actual exposure (dose) level. If the MOS is large, then typically, no additional study is needed. On the other hand, if the MOS is below one, then more detailed study could be done to refine the dose- or concentration-response and/or refine the actual exposure in the field. The acceptable MOS may be defined by existing criteria (e.g., water quality standards). If criteria do not exist then new guidelines for selected stressors may be warranted or, where necessary, determined on a location- and case-specific basis by the decision makers. Consideration should be given to background concentrations and consistent methods for site-specific criteria where possible.

Hazard-based research. Toxicity studies may be needed when data is insufficient to assess the hazard. Tools available today can inform this process, though some updating, or advancement may be necessary. Where experimental methods are not available, research may be needed to develop the assay and address the concern before a decision can be made to proceed. Danforth et al. summarized a workshop that was convened to consider knowledge gaps and research needs.187 Experts at the workshop identified the need for effects-based testing of produced water, including whole effluent assessments, and concluded that existing frameworks and approaches can inform advancements in produced water toxicity assessment strategies. It was also concluded that research is needed to assess acute and chronic toxicity and long-term risks specific to land application of treated produced water, noting that tools for toxicity analysis in aquatic environments are far more advanced and applied than those for terrestrial environments.

In addition to the lab-based research, efforts will be needed to translate the output of the new assays for use in decision-making-frameworks and guidance for stakeholders. Recently, in an attempt to move away from time- and resource-intensive traditional toxicity prediction assays that rely on animal studies, research has instead begun to focus on high-throughput assays that identify molecular initiating reactions.188 These molecular reactions may or may not result in organismal disease; therefore, further research is being conducted on how adverse outcome pathways can be developed and used to predict toxicity based on relevant initiating reactions.189

More robust research programs could be facilitated by development of a standardized sampling and handling protocol and a centralized repository to manage distribution of produced water samples. Such developments would provide real-world samples for the research community and facilitate comparison across studies and data sets.


Research Task: Risk characterization

Risk characterization is the final step of the risk assessment process for both ecological and health risks. This step integrates information from all preceding components of the risk assessment and synthesizes an overall conclusion about risk that is useful for decision makers. It will account for the treatment that is planned in Phases I and II above, and the extent to which treatment is expected to reduce the concentrations of stressors in the produced water intended for reuse.

Example: Assessing Risk to the Aquatic Environment. What are intended protection goals associated with produced water discharges?

- Prevent aquatic or soil toxicity impacts to the receiving environment;
- Prevent violation of applicable narrative or numerical ambient quality standards or criteria;
- Prevent endangerment of a drinking water supply;
- Prevent aquatic or terrestrial bioaccumulation to the extent that would threaten human or wildlife health.

How can risk-based permit limits and monitoring requirements be logically developed?

1. Define site-specific produced water quality characteristics.
2. Define applicable environmental quality standards for stressors that are intended to protect intended uses by aquatic or terrestrial wildlife and humans.
3. Conduct initial risk screening of relevant stressors by comparing predicted exposures to environmental quality standards to determine “reasonable potential” for potential risk.

The results from this analysis are used to decide if each quality parameter evaluated poses:

a) low potential risk;

b) uncertain risk due to either no or insufficient quality data; or

c) unacceptable potential risk.

For parameters designated as a) no permit limits are imposed but potential monitoring requirements may be considered to ensure acceptable produced water quality is maintained.

For parameters deemed as b) monitoring requirements are stipulated to refine risk evaluation to determine the need for further permit limits and/or monitoring requirements.

For parameters judged as c) permit limits and monitoring requirements are promulgated.

What produced water treatment is required?

Once permit limits are established, the required treatment technologies for ensuring acceptable produced water quality to support reuse can be evaluated taking a number of considerations into account, including cost, reliability, energy use and waste. See Phase IV for more on this process.
Phase IV Overview and Goals: The Risk Management and Decision Making step will make use of existing and to-be-developed criteria for stressors and receptors of interest. The criteria essentially establish an exposure level that is expected to be low enough to protect valued receptors, e.g., human health, aquatic organisms, livestock, crops or soil. Criteria will already exist for some chemicals of concern that may be present. But for individual constituents of concern that do not have existing criteria, the risk assessment will be helpful for determining what the new criterion should be for each type of receptor.

Final evaluation, practical considerations
As mentioned previously, even where health or ecological risk is deemed acceptable, other considerations such as economics, logistics, or public perception, may result in a decision not to proceed or to modify the proposed project in some way above and beyond that dictated by the risk characterization or regulations. Therefore, at this stage in the assessment, it will be important to look back at the considerations and more thoroughly analyze their potential impact on risk assessment, management, and a decision to proceed with the proposed project.

Decision: Is risk expected to be manageable?
This decision phase takes into consideration the knowledge gained throughout the assessment to determine if the risk is manageable, recognizing that appropriate controls will be incorporated through best practices and permitting requirements that will be applied to the project.

It’s important to recognize that a decision on whether risk is manageable and acceptable has several facets. A primary consideration is to whom the risk is considered acceptable or manageable, and by what standards. For example, a rancher or farmer may be concerned about risk to their crop or livestock from an upstream discharge of treated produced water but may not have any authority or input to influence a decision on whether that practice proceeds. It will be important to consider and address all stakeholder concerns as appropriate.

If risk is considered manageable to the decision-maker, the process should move forward to the establishment of the management strategies required. A key factor might be the outcome of risk assessment on treatment effluent as discussed in Phase III. If a conclusion is drawn that concern regarding the treated effluent remains significant, it may be appropriate to consider advanced or additional treatment options, as noted in the framework.

Research/Action Task: Establish practices and policies for further managing risk
There are a variety of mechanisms for further reducing and managing risk beyond treatment requirements. Where new programs for the treatment and reuse of produced water are developed, risk management strategies for ensuring that protective objectives are met and maintained are vital to avoid unintended consequences. Some important considerations for risk management include:

- **Standards.** A need to develop new or modified quality standards and/or permit limitations
to address constituents of concern may be present depending upon the reuse context. Data from research and risk assessment phases will be vital in informing standard development, and collaborative information sharing may help to make this process more efficient. Standards also provide a secondary point of information to inform treatment technology goals and objectives. The development of a new standard may also call for the development of an approved analytical method in some cases. Standards to consider might include:

- Effluent limitation guidelines
- Water Quality Standards
- Total Maximum Daily Loads (TMDLs)
- Drinking water Maximum Contaminant Levels, Action Levels, secondary standards or health advisories
- Irrigation standards
- Land application standards

**Monitoring Tools.** New or modified tools for monitoring can complement standards for newly developing or expanding reuse programs and may allow for ongoing learning while also supporting forward movement to pilot, study, and implement new projects. There may also be opportunities to define constituents of concern that should be monitored in early project/learning phases that may not be tied to permit or standard limitations. Established monitoring requirements can help ensure that permit requirements are consistently achieved by the permit holder. Guidance should also be provided for when monitoring data indicate permit requirements are exceeded, such as during transient upsets in treatment. Tools that might be considered include:

- Whole effluent toxicity assessment tools or similar bioassays
- Soil or crop monitoring tools
- Downstream monitoring stations
- Influent monitoring to identify unexpected changes

**Best Practices.** A number of best practices may be identified to further reduce potential risks and may not be tied to specific water quality limitations or standards. Best practices could be implemented by the operator, defined in guidelines by a regulator, or put into practice by an end user. Best practices are often situationally specific, but general guidelines may have wide applicability in some instances. There are numerous examples that may be considered:

- Preventing or limiting runoff
- Utilizing drip irrigation
- Implementing buffer zones, nutrient management plans or improved riparian areas near water bodies
- Rotating land application sites based on soil moisture content and crop uptake capacity
- Crop nutrient plans
- Selection of crops based on contaminant uptake/salinity tolerance
- Ongoing communication with community stakeholders
- Batch or truck sampling at delivery to treatment facilities for unexpected quality changes

**Information Sharing, Reporting, and Disclosure.** As reuse scenarios are more widely implemented, information on their success and lessons learned should be made openly available not only to local governing agencies, but also broadly to inform decision-making in similar circumstances in other regions. Additionally, reporting and disclosure of changes in oil and gas operations, such as key changes in chemical additive packages that may impact the quality of produced water, may be important to proactively address and manage any new or modified risks.

- One example of this type of reporting occurs in California, where entities that use produced water to irrigate crops report the chemicals used in the production of oil through the issuance of a
13267 order to the Central Valley Water Board. The Central Valley Water Board published responses to the 13267 orders on its website. The Board can issue additional 13267 orders in the future if necessary. This information is taken into consideration in the regulatory programs and in the Central Valley Water Board’s ongoing Food Safety Panel.

At this stage, as risks are identified, understood, and managed through treatment alongside established practices and policies for further reduction, decision-makers may conclude that a research program should proceed.

**Research Task: Ongoing assessment and incorporation of new knowledge**

Available monitoring data, new knowledge, new tools, and other pieces of information should be incorporated into adaptive management and ongoing assessment strategies. If new risks or risk management opportunities are identified, they should be considered in future revisions or iterations on programs, guidelines, or best practices.

Research partnerships between academia, industry, agencies, end-users and other stakeholders should be promoted. A process of continuous improvement to further identify and reduce reuse risks will be better informed by gathering the most current data and information available. As new data are reported, methods are developed, standards are considered, etc. programs for reuse that can be rapidly adaptable to accommodate new information can result in outcomes that even further reduce potential risk to environment and communities.

Dedication to a transparent, iterative process of learning and advancement with a shared goal of encouraging reuse while reducing risk to the furthest extent practicable will help to support expansion of reuse opportunities as well as stakeholder support.

**Fit for Purpose: Research Questions and Other Considerations for Varied End Uses**

Not all produced water end uses will require the same analysis. In fact, the benefits, risks, and costs associated with reuse scenarios will differ based on the produced water quality and unique circumstances of the end use. Not all questions will be appropriate or necessary for all end uses.

This section presents examples of research questions and other decision-making considerations by end-use types. Examples are illustrative rather than exhaustive, providing a representative overview of “fit-for-purpose” issues that may arise within a decision-making process.

Issues presented are likely to be worthy of research and investigation by interested parties.

**Land Applications**

Land application scenarios will demand understanding not only of the basic constituents of concern, but also information like concentration, expected uptake rates of ground cover or crops, long-term considerations for soil, and how to prevent harmful chemicals from entering the food supply or water resources at harmful levels. Important research questions or considerations may include:

- What specific constituents may be present at levels of concern for the specific land application or irrigation purpose proposed?
- What are the appropriate agronomic rates of key constituents for various food crops or cover crops to reduce groundwater impacts?
- What are rates of absorption, infiltration, permeability, percolation, etc., in various soil types with various ground cover?
- What best practices or other steps must be taken to limit runoff? What constituents may remain on the surface or at shallow depths that may impact runoff?
- At what rates do irrigated land or crops

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190 California Water Code 913267 and 13267.5.


192 California Central Valley Water Board, Oil Fields – Food Safety, [https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/](https://www.waterboards.ca.gov/centralvalley/water_issues/oil_fields/food_safety/).

193 Agronomic rates are most commonly referenced with respect to beneficial use rates for biosolids and sludges. It refers to the amount of nutrient (nitrogen) needed for the irrigation purpose and yield goals while also minimizing the amount that might pass below the root zone to groundwater.
uptake constituents of concern and are there lethal or sub-lethal impacts?

• Are there strategies for irrigation to reduce run off or other impacts, such as drip irrigation? What about irrigation in urban settings, such as for municipal golf courses, etc.?

• How can long-term impacts to soil biota and soil health be studied or modeled in order to make near-term, protective decisions?

• Assays and other high-throughput/whole effluent rapid analysis tools are limited in the terrestrial environment as compared to the aquatic environment (i.e., whole effluent toxicity tests). How can these tools be expanded to better understand impacts of complex mixtures on soil even where all the potential constituents of concern may not be identified?

• Are there any worker exposure considerations?

• What steps can be taken to reduce the risk of inadvertent consumption or exposure, such as to wildlife and the public?

• What is the resiliency of a receiving ecosystem to adapt to changes in water quality, and are there similar concerns if treated produced water was no longer available?

• Are there potential impacts to groundwater or surface water and how can they be prevented or mitigated?

Water Applications

Reuse scenarios that may impact water resources can come with a host of considerations, varying from impacts to a receiving water body (the water quality itself) to impacts on soils and sediment, aquatic species, surrounding ecosystems, end users, etc. Much of the issues associated with a water application will likely be considered in the permitting process. Considerations include:

• What studies are necessary to model fate and transport of constituents of concern for pathways of interest?

• What is known about the pathways of bio-accumulation, and are there any media (i.e., soils) or species (i.e., fish) that may be more susceptible?

• Understanding the impacts of changes to quantity as well as quality in a water body is critical prior to introducing a new source. Areas for study might include:

  • Impacts to bio aquatic life at various increased flow rates? Impacts of reduction or removal after flows subside?

  • Is there a point where the aquatic community or environment becomes stressed?

  • What is the ratio of discharged flows to other existing flows and does that potentially create an ecosystem impact? How does this differ between an aquifer, river, intermittent stream, seasonal flow, etc.?

  • What is the background level of stressors relative to quality objectives?

• Understanding the impacts of changes to quantity and quality in a ground water aquifer is critical when considering managed aquifer recharge or aquifer storage and recovery. Areas for consideration and study might include:

  • Impacts to wells in the area (irrigation, livestock watering, household wells, etc.);

  • Impacts to movement of water in the aquifer (movement of contamination plumes, changes in quantity and quality of ground water outcropping); and

  • Chemical reactions in the geological formation after injection.

• Understanding the assimilative capacity of a receiving body or aquifer will impact volumes and constituent levels allowed for discharge or injection for reuse based on dilution, mixing, and other factors. Questions include:

  • Impacts to wells in the area (irrigation, livestock watering, household wells, etc.);

  • Impacts to movement of water in the aquifer (movement of contamination plumes, changes in quantity and quality of ground water outcropping); and

  • Chemical reactions in the geological formation after injection.

194 See, e.g., USEPA, Whole Effluent Toxicity Methods, https://www.epa.gov/cwa-methods/whole-effluent-toxicity-methods (noting that, “Whole Effluent Toxicity (WET) refers to the aggregate toxic effect to aquatic organisms from all pollutants contained in a facility’s wastewater (effluent). It is one way we implement the Clean Water Act’s prohibition of the discharge of toxic pollutants in toxic amounts. WET tests measure wastewater’s effects on specific test organisms’ ability to survive, grow and reproduce.”).
• What are the designated beneficial uses of the water body or aquifer and will they be impacted?

• What are the characteristics of the receiving system? Will water flow downstream and mix with other discharges or into a lake or other end “sink” where the water is held for a longer period? Do constituents of concern vary based on fast or slower moving systems?

• What impacts are there to other uses due to injection for managed aquifer recharge or aquifer storage and recovery? Will the injection of treated produced water increase the quality of the aquifer and thus change its classification from “saline” to “marginal” quality or from marginal quality to USDWs?

• Will the receiving body allow for a large dilution and mixing rate, or will the discharged treated produced water make up a majority of water flowing into an intermittent stream or water way? What are the impacts of the proposed discharge to the receiving body?

• What additional considerations are necessary to ensure that flows and quality levels are acceptable to maintain designated beneficial uses?

• Crossing of regulatory boundaries may complicate the permitting of produced water discharge and reuse. Questions may include:

  • What are the implications of discharges into a water body that may cross jurisdictional boundaries?

  • What are the implications of the injection of treated produced water into a large aquifer that lies beneath multiple states?

  • Is there a process to resolve conflict that might arise through the transfer of water across jurisdictions for various purposes?

  • Who owns produced water and does that change if it becomes a product rather than a waste?

• What agencies may need to be involved?

• What are the differences in the regulatory controls and transboundary transfers if produced water is reused through direct application, aquifer recharge, or surface discharge?

• Considering impacts on a broader watershed or water system will be vital in understanding not only the appropriate limits for a specific treated produced water discharge or aquifer injection, but also the implications on the larger system due to a new industrial discharge coming online in a region. Permit conditions may be established based on upstream and downstream conditions, and limits derived from Total Maximum Daily Loads (TMDLs) may be applicable to address impairments for specific constituents. If conditions change, there may be broader long-term considerations for future permitting.

Surface water examples include:

  • What implications may occur for other municipal or industrial discharges if flow or character of upstream or downstream segments changes?

  • Are new numeric or narrative permit limits appropriate?

  • Could treated produced water discharges improve the water quality conditions or create additional impairments?

  • Would there need to be a change in the biomonitoring species for other discharges in the water body or stream segment, and what would the appropriate species be?

  • How does ionic balance or mineralization change in a stream segment and are there implications for other discharges?

Groundwater examples include:

  • What implications will there be for other injection sites in the aquifer with the addition of a new injection point and source?
• Will there be a need for volume reduction or enhanced treatment for others injecting in the aquifer?
• Is there an adequate and appropriate method to account for treated produced that is expected to be recovered for later use?
• Discharges may eventually find their way to a water body used for a public or private water supply or designated for emergency water supplies. Therefore, potential risks for drinking water treatment facilities, such as the formation of disinfection byproducts, altering the basic water chemistry causing corrosivity concerns with lead and copper, and other general scaling or fouling of equipment should be considered.

Lessons from Historic Practices. In some cases, both historic (e.g., unconventional produced water treated by POTWs and some CWTs) and relatively recent and ongoing (e.g., conventional sources to CWTs) permitted discharges have been shown to have negative consequences — often due to inappropriate or inadequate treatment specifically for produced water. Studies of such impacts present valuable learning opportunities, and some improvements can be seen where regulatory programs and industry practices adapt to identified challenges.* Studies such as the few highlighted here are not exhaustive, but do help to underscore the importance of careful consideration of the quality of different influent streams, appropriate fit-for-purpose technologies, and permitting programs in order to avoid unanticipated short and long term impacts in the future.

One identified challenge has been the management of compounds like radionuclides that can bioaccumulate in biological systems or selectively partition into the sediment in ways that aren’t always easy to predict. For example, a recent study has found strontium accumulation in the shells of freshwater mussels, which are hypothesized to indicate a long-term impact of historic surface water discharges in Pennsylvania.** The authors indicate a next step will include a soft tissue investigation to better understand whether there may be impacts higher up the food chain for animals that may feed on the mussels. A second study in Pennsylvania focused potential ongoing impacts from discharges of treated conventional produced waters that continued after state limitations were made on unconventional produced waters in 2011, and found accumulation of radioactivity in sediment near discharge sites from 2014–2017 that far exceeded radiation in upstream sediments.† This and additional studies at Pennsylvania sites have also indicated that stream chemistry, which can make radium less bioavailable, can also make it more mobile and may lead to elevated concentrations of radium above background levels downstream.‡‡ Studies have also measured elevated radium levels at discharge points in Wyoming, where produced waters are typically much lower in radioactivity.‡ Overall, studies such as these emphasize the opportunity to utilize research to learn and adapt practices to reduce impacts that may have been unforeseen, although the scale of historic and ongoing impacts and how these elements may be mobilized, is still under study and worthy of further investigation. A key challenge is interpreting such information in an objective, risk-assessment context.

* William D. Burgos, Luis Castillo-Meza, Travis L. Tasker, Thomas J. Geeza, Patrick J. Drohan, Xiaofeng Liu, Joshua D. Landis, et al., “Watershed-Scale Impacts from Surface Water Disposal of Oil and Gas Wastewater in Western Pennsylvania,” Environmental Science & Technology 51 (15):8851–60 (July 12, 2017), https://doi.org/10.1021/acs.est.7b01696 (showing through core studies that studied sediment impacts correspond to years prior to regulatory change and decrease over time); see also Van Sice et al., below, which found that loading of radium at discharge sites decreased by an estimated 95% after unconventional discharges at the studied sites ceased.


Industrial Applications
Treating and reusing produced water as a source of intake water, or feed stream, for industries may provide opportunities to reduce fresh water consumption or supply raw materials. However, significant considerations may be necessary to ensure that changes in water source or feed streams do not inadvertently have negative implications for industrial outcomes or operations. Some of these may include:

• Process implications due to a change in the character of source water, such as scale deposits in piping or other units, cooling towers, pumps, etc.;
• Modifications in the character and required management and disposal of residual wastes, sludges or used fluids;
• The need for additional pretreatment before use;
• Changes in effluent that may result from influent changes and the potential for necessary permit modifications to monitoring limits or discharge allowances under existing permits due to a change in conditions;
• Market considerations for the use of products mined from produced water – i.e., lithium, salt – and whether market values may be modified by an influx of product locally or nationally; and
• Worker safety and exposure considerations for handling new water sources or feed streams and others.

Case Study: Soil Considerations in Oklahoma. The Oklahoma Conservation Commission (OCC) has a program on Healthy Soils and shared some perspective on healthy soils and produced water, adapted here from an email. Healthy soils have greater capacity for water infiltration, reduce erosion, and reduce need for fertilization and pesticides, thereby protecting water quality and restoring a more natural watershed. Five basic principles that support soil health include minimizing disturbance, maximizing plant diversity, maintaining a live plant root, maximizing vegetative cover, and integrating livestock. For the soil health program (or conservation programs in general) to support the use of produced water application to agricultural lands, questions need to be answered, including:

• Salinity: Many agricultural fields in Oklahoma already are challenged by areas of high soil salinity. Areas with the greatest need for irrigation may already have higher than desired salinity due to current and historical irrigation. Also, as irrigation technology improves to deliver more water to the plant than the atmosphere in the field, there is potential for mineralization to impact piping and delivery sprayers. Before most producers would be comfortable with produced water application, they would need to see regional demonstrations as well as studies showing how various crops would be affected during various environmental conditions, e.g., if irrigation is done during a dry period vs. a wet period and, how are plant growth and soil salinity affected? What produced water application rates in various regions, soil types, and weather patterns result in no significant decrease in vegetative growth or increase in erosion rates? How would irrigation with or land application by produced waters affect healthy soils vs. soils with lower organic content and biological activity?

• Producer and public concern: Although produced water differs significantly from hydraulic fracturing water, many people will be concerned with the potential for production chemicals as well as the natural petroleum compounds, heavy metals, radionuclides, and other dissolved and volatile organic compounds contained in the water to impact or be accumulated in livestock, crops, or other vegetation. Studies and demonstrations will need to evaluate how this can be safely done with minimal risk, but also preferably with some benefit to the agricultural operation. Many agricultural producers will only accept a practice after it has been demonstrated to them that it works in their region, with their soils, climatic conditions, and type of agricultural system.

• Environmental impacts: The agricultural industry is already heavily scrutinized for their potential and real environmental impacts. Many farmers, agricultural product users, as well as conservation professionals will be concerned with the results from land application of produced waters and what impacts that will have on downstream water quality. Questions will need to be answered with respect to where, when, and how much land application of produced water has no measurable impact to runoff water quality.
Livestock, Wildlife, and Other Consumption
Studies in literature address the potential implications for livestock and other wildlife from consumption of different pollutants, minerals, constituents, water, etc., although few are directly devoted to treated produced water (see “State of the Science: Literature Review”). Specific considerations include:

• How best to determine safety of certain treatment levels for a variety of consuming species?
• What does literature say with respect to salinity and TDS levels? Are those studies fitting or appropriate for the receptors of interest?
• Are there potential chronic, sub-lethal effects that should be taken into consideration? If so, at what levels?
• Are some species more susceptible to toxic effects or bioaccumulation? What potential food-chain considerations may be at play for higher order species?
• Are there ecosystem considerations if discharges are not long-term, sustainable, or reliable?

Other Practical Considerations and Research Opportunities
For any decision on produced water treatment and reuse, many considerations are at play above and beyond scientific research on health or environmental risk, including laws and regulations, public perception, logistics, economics, and additional environmental considerations, as well as the anticipated benefits of the reuse. Analysis of these broader costs and benefits is likely to occur before or alongside risk-assessment research. Alone or collectively, these additional considerations can be decisive. Study of these topics may be called for in the near-term as progress is made on treatment technologies as well as health and environmental considerations.

Content for this section was developed in collaboration with industry and regulatory project participants who contributed to brainstorming on priority issues. The ideas shared here are illustrative, but not exhaustive.

Legal and Regulatory
Many considerations related to law, regulation, permitting, and policy are covered in Module 1 of this report. Following are a few key considerations related specifically to the decision-making process for reuse or release outside oil and gas operations.

What permits or authorizations may be required?
While it is possible that some reuse scenarios may not require permits, permitting and authorization will be a major consideration for many reuse strategies, particularly where existing permitting or regulatory structures and guidelines are limited. Permits or other authorizations may come into play at the federal, state, and even local level depending on the proposed project and may be required from multiple entities. For pilots and full-scale practices, impacts of these authorizations can range from determining whether, when, where, and how a practice can proceed at all, to defining the data and information necessary to establish limits or monitoring requirements. Data limitations may present challenges for permit writers in crafting permits that are confidently protective of human health and the environment. Permitting and authorization structures must also tackle a wider range of considerations, including:

• What agency or agencies have authority? In many states, current regulatory language or memorandums of understanding between agencies do not clearly define who may have the authority to control or permit a given alternative use. Different uses may result in different agency involvement and different authorities, regulatory programs, or permits may be required for multiple stages of a proposed project, from storage and treatment to transport and final use. Some are working through these questions, including Colorado, Pennsylvania, Oklahoma, and New Mexico.

• Who has ownership or water rights for produced water, treated water? Clarifying who owns the water, what it means to take possession/custody of water, and whether there are valued water rights attached to a ‘new’ water available for use is a vital prerequisite to moving forward on a project. In many states, these issues are not currently settled in the context of produced water but are likely to play a significant role in decision-making due to the impact a particular result may have on everything from reuse authority to economics...
and liability. States may reach differing conclusions on these questions.

- **How is produced water defined?** Whether produced water is considered a waste or a resource, surface or groundwater, mineral or non-mineral, etc. will play a role not only in permits and authorities for reuse projects, but also in economics. For example, might a produced water treated for sale and use outside oil and gas operations — and therefore, transitioned from waste to valued resource — require a royalty payment to a mineral or surface owner? These questions are not yet fully answered.

- **Are additional permits necessary to implement reuse, i.e., infrastructure?** Reuse scenarios that involve transport outside oil and gas operations are likely to require new or expanded infrastructure like storage, transportation, and treatment facilities. This infrastructure may often require permitting, and the timelines and requirements for such infrastructure may play a significant role in whether and when a project moves forward.

*Who has liability and is liability transferred?*

Liability is a significant consideration in scenarios of treating and reusing produced water outside oil and gas operations. Views vary widely within the oil and gas industry as to willingness to assume liability and within regulatory authorities as to where liability may or may not change hands in reuse scenarios. Concerns regarding both short- and long-term liability play a major role in decision-making on whether to move forward with a project. Some companies may be satisfied that liability and ownership is likely to transfer to a third-party treatment company or final users, while other companies’ legal departments may put higher hurdles in place due to the risk that longer-term future impacts (like soil degradation over a decade time frame, or newly discovered contaminants of concern not previously analyzed or limited) may be traced back to the company. There are also potential concerns with basic liability for waste management (where produced water is classified as a “waste”), and what may occur when produced water leaves oil and gas operations and the third party with custody of that waste mismanages it. The way in which liability is assigned may impact how or whether certain reuse projects proceed.

Numerous other legal and regulatory considerations may require attention, analysis, and adaptation if alternative uses are to be considered more widely in the future. Some are discussed in more depth in Module 1, and others may not yet be identified.

**Public Perception**

Public perception is an undeniable consideration not only for oil and gas activities in general, but also for reuse of any wastewater, not just treated produced water. Local communities are often extremely active when it comes to protection of natural resources. Where scenarios may be in place to release treated produced water for reuse in ways that may have a broader set of potential impacts, like watering crops or local road application, public perception is likely to play a major role in the way decisions are made.

*Just as research and risk assessment will need to be conducted in a localized, site-specific way, so too will public communication and perception management.*

How to best manage public perception will depend on local dynamics and pressures. In some regions, public perception may involve a balance between concerns over current produced water disposal options like disposal wells and newer proposed alternatives for treated produced water like discharge or agricultural use. For example, local communities with significant concerns regarding induced seismicity, may be more open to consider reuse opportunities. The same may be true for communities facing drought intensity or fresh water scarcity. Where options are limited, the public may be more open to consider alternatives, though transparency and communication will still be key. There have been a few limited studies of public perception specific to the reuse of “desalinated” produced water (broadly defined in participant interviews as “a process by which salt and other contaminants are removed from the water”) for various purposes both inside and outside oil and gas operations. These studies, conducted in Texas and Pennsylvania, have concluded that familiarity with technology results in greater comfort with reuse, and that respondents are generally more “favorably disposed” toward
reuse options that reduce the probability of human or animal ingestion.195

Public perception, concern, and attention regarding produced water and wastewater reuse — even if heightened due to association with oil and gas development — is not unique to this industry. In fact, one of the leading challenges of wastewater reuse internationally is public perception, as projects on other types of wastewater reuse have demonstrated.

• **Risk communication is vital.** Beyond a one-way conversation to educate stakeholders, risk communication entails a two-way opportunity to gather information on perceived risk and to deliver information that addresses concerns. Clarity and care in messaging are important.

• **Mitigation measures should be clearly explained.** In some cases, it is helpful to present information about the barriers and mitigation measures available to increase the safety of reuse. A barrier might include natural or artificial dividers between a discharge and an eventual end-use such as rivers and streams or constructed impoundments or wetlands. Such measures can modify perception of the immediacy of impact and better incorporate a treated discharge into a larger water system.

• **Transparency is key.** Data and information sharing of any and all evidence that a wastewater can be safely or successfully reused is relevant and informative to public perception. Transparency is vital and data from labs to pilot scale fields studies should be shared, even where results indicate more work needs to be done. Stakeholder acceptance can be increased through transparent communication and collaboration with local scientists, politicians, and other business or social leaders.

For municipal wastewater treatment plant effluent, constructing buffers between where the water is generated or treated to where the water enters a surface water body or ground water aquifer either through percolation or injection has led to much greater acceptance. For example, the North Texas Municipal Water District constructed a wetland for the treated effluent to flow through prior to entering a lake. Walking paths and a water education center were constructed in the wetlands area allowing the water district to educate the public about water, its uses, treatment, and beneficial reuse. Additionally, a new space was created for use by school groups and civic organizations that ultimately helped gain acceptance of the reuse concept.196 Oil and gas companies and regulatory agencies may find this model useful in gaining public acceptance of a given discharge or reuse project, particularly in more urban areas.

Public concern can be a forceful motivation to change or modify decisions on produced water reuse outside oil and gas operations and should be addressed as early as possible in any proposed project. Public involvement or perception not only will relate to health or environmental risks but may also relate to increased infrastructure required for extensive reuse projects like trucks, pipelines, impoundments, or treatment facilities. In California, public concern and questions regarding health and environmental impacts of reuse have led to demand for significant new research and action.


196 [https://www.ntmwd.com/](https://www.ntmwd.com/).
Agricultural Reuse of Produced Water in California. California produced approximately 175 million barrels of oil onshore in 2016, along with nearly 2.73 billion barrels of produced water. Interest in produced water reuse has grown due in large part to the ongoing drought. Reusing produced water in irrigation, which has occurred in eastern Kern County for over three decades, has expanded in recent years. Produced water here contains low concentrations of total dissolved solids and boron, making reuse more feasible than in areas with higher salinity.

Concern over produced water reuse for agricultural irrigation has arisen in recent years and prompted the Central Valley Regional Water Quality Control Board (Central Valley Water Board) to develop a Food Safety Expert Panel (Panel). The Panel’s purpose is to guide sample collection and analytical methods for field studies, assess results, identify data gaps, and procure practical outcomes regarding produced water management. The Central Valley Water Board will consider the Panel’s recommendations to regulate produced water reuse. Panel meetings are typically held quarterly and are open to the public. The meetings are attended by industry and environmental stakeholders as well as regulators.

In the three years since the Panel’s inception, multiple crop sampling events and an irrigation water quality evaluation were conducted in vicinity of the Cawelo Water District, where produced water is currently reused to irrigate crops under a permit issued by the Central Valley Water Board. The Central Valley Water Board has also received chemical disclosures from operators and suppliers through informational orders (California Code § 13267). These disclosures are available to the public on the Central Valley Water Board’s website and are being evaluated and incorporated into future sampling efforts. The oilfield chemical additives evaluation is ongoing since several chemicals do not have standardized sampling methods, making water monitoring and crop plant uptake quantification difficult. However, community representatives and Panel members share an interest in evaluating and quantifying chemical additives when feasible and conducting health risk evaluations before the Panel provides its final recommendations.

Logistical Considerations

Any new produced water management option, especially involving reuse outside oil and gas operations, will require the operator, end user, and any midstream third-party to consider logistics. These should likely be assessed early in the decision-making process because they may significantly change the economics or feasibility of a project.

- **Timing.** In some cases, reuse will be practically or economically feasible only where the new water supply coincides with local water demand. Even where demand is present, many end users require long-term, reliable, consistent quality water supplies, particularly if they may be making business decisions to move away from another reliable source.

- **Infrastructure.** Depending on the location of an end user relative to produced water sources, new or expanded storage and transportation options may be required. Additionally, meeting a variety of water quality requirements will necessitate treatment facilities and
related infrastructure not only for the treatment technologies themselves, but potentially also for residual waste management (like landfills). Such infrastructure needs not only impact economics of particular reuse scenarios, but also play a role in public perception as well as risk, and liability for potential issues like spills. Where produced water transport occurs, practices for loading, unloading, pipelines, etc. aimed at reducing or preventing spills should be considered and incorporated. For operational reasons, and to reduce transportation risks, produced water is likely to be treated near the source.

- **Operational decisions.** The end use planned for produced water may have an impact on upstream operational decisions. For example, operators may design drilling or hydraulic fracturing chemistries to avoid using or creating a chemical of concern that is challenging or costly to remove through treatment and poses a risk to the environment or health if released. Or, companies may decide to invest in water treatment rather than constructing disposal wells in certain areas. Operational decisions may also demand modification for end users. For example, a farmer or rancher interested in the potential to use treated produced water may consider planting a different type of crop.

**Economic Considerations**

Economic considerations come into play for any produced water management scenario. Even where scientific studies, regulations, liability, and public perception point to the feasibility of reuse, cost is likely to be a deciding factor. Industry operators will have to convince their business units that reuse will create value relative to status quo produced water management, while end users will need to be convinced that using treated produced water is an economically sound and reliable alternative for their use or business. The question, on a case-by-case basis, will be whether benefits or opportunities outweigh the price tag. In some cases, opportunities for reuse may come with opportunities for economic gain.

Economic considerations regarding produced water management are addressed in Module 2 and a discussion of water rights related to reuse is included in Module 1. Additional considerations relevant to reuse outside oil and gas operations include:

- **Treatment.** Treatment is an obvious economic consideration for alternative uses that demand high quality waters. Advanced treatment can be costly, though there are some technologies in development with promise of significantly reducing that cost and can skew economics away from reuse unless there are cost or incentives to offset the price differential between disposal or in-field recycling and a use outside oil and gas operations.

- **Transportation, infrastructure and logistics.** Storing, moving, and managing produced water and treated water for reuse outside oil and gas operations requires investment in transportation, infrastructure or other related logistics. Infrastructure will require upfront investment, which may or may not be annuitized over the life of a well (because water may not be produced consistently). Economics on logistics and infrastructure may demand long term commitments or multi-operator cooperation, adding not only cost but operational and financial complexity. Cost and logistics for storage and transport (as well as risk and permitting requirements) will likely vary significantly for treated versus untreated produced water. For example, produced water treated to meet Pennsylvania’s “dewasting” standard can be stored and transported like fresh water prior to being used to develop or hydraulically fracture an oil or gas well, which can reduce both risk and logistical costs (though that must be balanced with the economics of treating to that standard). Cost analyses of transportation infrastructure such as pipelines will consider the value of the water for the end user. The Oklahoma Produced Water Working Group report found that the value of water to users is often dramatically less than the cost to
transport it. This dynamic is one reason why discharge to surface water may be investigated prior to long-distance pipelines as a delivery mechanism for reuse.

- **Contracts, agreements, long-term commitments, royalties, and ‘sunk costs’.** The basic decision to change an existing practice for waste management can itself come with a cost. In many cases both operators and potential end users have existing contracts or agreements for the purchase and use of water resources, many of which may be long-term or tied to production rights on a lease. If these costs are already “sunk,” the economics of looking at alternatives are impacted. Additionally, water supply is increasingly tied to surface use agreements between operating companies and surface owners. This can create additional challenges.

### Example: Contracts and Agreements

Pioneer Natural Resource and the City of Midland entered into a contract in 2016 for Pioneer to take and pay for treated municipal water for use in oil and gas development. The full project, including treatment plant upgrades is estimated at $133.5 million. The Midland contract is volume based with a primary term expected to last for 20 to 28 years depending on flow rates. Pioneer has a similar contract with the City of Odessa with an 11-year, $117 million term.

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Long-term commitments are also a consideration when it comes to contracting with a third-party treatment provider. Many such providers may ask for multi-year agreements to either provide or purchase water in order to manage operational economics, but such agreements may be risky for operators (if regulation changes, downturns reduce produced water volumes, operators are sold, etc.) or end-users (if quality changes impact business, regulation changes, etc.).

Potential economic risks are also associated with uncertainty surrounding the regulatory classification of treated produced water as a waste or valuable product. For example, produced water is treated as an oil and gas related waste today and operators carry the cost of managing and disposing of that waste. If produced water were to become a valuable product, it is unknown whether a new cost such as a royalty may be attached.

- **Energy.** Energy demand and supply could play a major role in decision-making for reuse alternatives, particularly where heat- or power-intensive treatment technologies are required. This consideration requires not only an analysis of the cost of power, but also the cost of getting power where it is needed, such as the costs of generators or transmission lines. Research should be done to better model implications on energy demand, supply, and cost for reuse scenarios. Additionally, investigation of the opportunity to utilize waste energy or co-located renewable energy resources is appropriate.
• **Markets.** Markets factors are likely to be unpredictable. For example, while the perceived or predicted market for solid products often play a role in current treatment technology expected valuations, those markets may not actually exist in a region, may change drastically over time with the influx of new product quantities, or may not be viable if solid products are not proven to meet purity standards and regulatory requirements. The products produced and potential hazards (particularly transportation risk) should be reviewed. Another example is the market for water and water rights. Facilities that may accept and treat produced water for surface discharge may seek opportunities to gain an additional income stream from the creation of new water rights. This will require not only a market and user for that water, but also a regulatory structure for prescribing a value to treated produced water – neither of which exist in most states today. If fee structures for third-party water managers or treatment providers incorporate theoretical rebates for monetary benefits gained from the sale of products on market, operators may not be willing to take that risk, or may not recommit in the future.

• **Solids management.** Advanced treatment of produced water, in many cases, will result in large volumes of residual solids unless systems are designed to avoid this outcome (i.e., produce a heavy brine waste stream for injection). Some of these may be marketable if of pure quality and permitted, but this may not always be the case, and may not be a reliable long-term business plan. Large volumes of salts would also have to be transferred to the correct markets via rail, truck, etc. which impacts economic outcomes. Therefore, the volume of solids produced and considerations for its management will play a role in decision-making for alternative uses, particularly those that require distillation or crystallization. Solids management can have a logistical component, such as where large volumes of salts or other residual solids can be stored or disposed. On the other hand, solids management can also come with high cost.

• **Water rights.** Water rights are a key consideration with respect to reuse of produced water. See Module 1 for a more substantive discussion.
• **Relative economic feasibility.** Circumstances in specific regions may affect economic feasibility. Typically, oil and gas operations have low costs to source and dispose of water relative to the treatment and transportation costs that may be involved with advanced treatment and other logistics for reuse outside oil and gas operations. This was one of the major conclusions of Oklahoma’s produced water study.\(^{201}\) In eastern Pennsylvania, where there are few if any disposal wells and trucking costs hundreds of miles to Ohio are significant, economics supported investment in NPDES and centralized treatment for discharge. Another significant factor can be if a certain produced water is substantially lower in dissolved solids, which could greatly reduce the treatment cost. This example can be seen playing out in California’s Kern River oilfield through treatment for agriculture, although treatment cost is not the only consideration and studies regarding food-safety are ongoing. These atypical examples will likely be a guide to future locations where the economics of reuse outside oil and gas operations will be considered on a case-by-case basis.

**Other Environmental Considerations**

In addition to health or ecosystem impacts that may be associated with reuse scenarios, additional environmental considerations may influence big-picture decision-making on reuse options. These may include emissions from treatment technologies, managing waste materials from treatment, cumulative ecosystem impacts, endangered and threatened species considerations, or other specific or localized issues for an end use such as erosion or flow.

**Benefits**

In any analysis of risks, benefits should be accounted for as well. Assessment of benefits is particularly important where high costs or potentially significant risks are under consideration. In most scenarios, benefits related to water quantity will be a primary driver for investigating treated produced water reuse alternatives. For example, where water can be treated for surface water discharges, there may be benefits for water users both upstream and downstream due to increased volume in a stream or river. For industrial applications, where fresh water is traditionally used, use of treated produced water can displace fresh water use in the local region, leaving greater volumes available for other users. There may also be scenarios where ecosystem or habitat restoration may be a positive outcome. In addition, the treatment and reuse of produced water may reduce seismicity or pressure issues associated with underground injection and disposal. However, further work is needed to better determine how much benefits should be valued. There may also be benefits from extraction and recovery of various salts and minerals of value in produced water. Reuse also may support the ongoing viability of regional oil and gas operations at times when produced water volumes exceed available disposal capacities or other management options in the region.

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Treatment Technologies

This section provides a general overview of treatment technologies that may be necessary and beneficial for treating produced water for reuse purposes outside oil and gas operations.

Treatment of produced water is critical in achieving defined quality objectives for reuse. The interest in developing and testing various technologies for the treatment of produced water spans the academic, government, and industrial spaces. Produced water treatment presents unique challenges. It can contain TDS levels 5-10X that of seawater (~30,000 mg/L), have significant variability over time and geography, and contain potentially harmful and difficult to treat organic constituents and naturally occurring radioactive materials— all of which makes both treating the water and handling of the residuals a challenge.

TDS are a key consideration in selecting an appropriate treatment train because the presence of high TDS levels can, among other things, negatively impact the efficacy of a technology and greatly influence cost. Treatment challenges associated with TDS impact numerous established treatment processes from biological systems to membrane technologies. For example, in biological systems, high TDS levels impact the microbes used to traditionally remove dissolved organic carbon (DOC), prevent floc formation, and can simply halt non-halotolerant microbes completely.\(^{202}\) The cost, energy, and technological requirements for TDS removal can present a major challenge for produced water treatment. High levels of TDS not only prevent the use of conventional membrane processes, such as reverse osmosis (RO), but can also create significant solids management issues, even if water can be recovered utilizing select treatment technologies (i.e., thermal distillation). These examples illustrate the challenges associated with TDS from pre-treatment to the final management of residuals, demonstrating why TDS treatment and management are one of the main considerations for any produced water treatment.

Figure 3-12 below includes TDS as a primary axis in the overview of available technologies. The second axis focuses on removal capabilities for other constituents of potential concern.

Other constituents in produced water—including suspended solids, DOC, radionuclides, and metals—are challenging to remove on their own, with some becoming even harder to remove in the presence of high TDS levels. Their removal can be evaluated based on their size, particularly for membrane-based processes, as illustrated in Figure 3-12. Of these various constituents, some may be present as large particles, like suspended solids (>1 µm), or as small dissolved particles like aqueous salts (<0.001 µm).

Suspended solids (commonly TSS, or total suspended solids) are considered the largest inorganic constituents in produced water, and most treatment methods for suspended solids removal are not impacted by TDS (see Appendix 3-E). DOC can range in size from large humic substances (~0.1 µm) to low molecular weight acids or hydrocarbons (~0.001 µm). Unlike suspended solids, DOC removal with biological processes is significantly impacted by high TDS. Metals are small (<0.001 µm) and their removal can also be impacted by TDS, as select treatment processes utilize biological processes (packed bed biofilm reactor). Classic precipitation methods that rely on pH adjustments, can also be hindered by levels of alkalinity or hardness present, by requiring significant amounts of acid or base to adjust the pH to the appropriate levels. Radionuclides (or NORM), like metals, are also small, and present a unique challenge for produced water treatment. This is primarily due to NORM’s expected presence in treatment residuals that can significantly increase the cost of waste management and disposal.

An additional treatment consideration not covered in detail below is temperature. The assumption is that produced water will be treated at ambient temperatures. In some cases, depending upon the scenario, temperature can be a challenge because produced water temperatures are elevated when produced and after separation from oil and gas, which can detrimentally impact membrane treatment and biological processes.

Figure 3-12: Visual Representation of Treatment Technologies and their Average Capabilities for Removing Produced Water Constituents

This visual represents the average capabilities of treatment technologies to remove produced water constituents. It presents a selection of treatment technologies and is not comprehensive. The citations that support this figure are presented in Appendix 3-E.
Produced Water Treatment Challenges: Key Classes of Constituents

The following section describes several key classes of constituents in produced water that may present challenges for treatment to qualities necessary for reuse options outside oil and gas operations.

A substantive table reviewing current treatment technologies and known removal of constituent classes is shown in Appendix 3-E. The table includes information on each technology's current validation status; TDS range; removal capabilities for solids, organics, metals, and TDS; water and waste recovery; energy demand; and associated citations and references.

- **Suspended solids** in produced water consist of small solid particles, that are not dissolved, and remain in suspension. Produced waters can contain high levels of suspended particles and, a variety of technologies are applied for their removal. The most common is basic filtration, though there are other more advanced options. For example, dissolved air flotation is a treatment technology using fine gas bubbles to separate small, suspended particles that are difficult to separate through settling. Another example is coagulation/flocculation, which typically relies on metal salts to coagulate particles into larger solids that can be settled or filtered. These along with a handful of other technologies can and have been used for the removal of suspended solids in produced water treatment. However, the removal of suspended solids in produced water can still present challenges, with the coagulant/flocculant doses needed for suspended solids removal varying greatly from water to water, even for the same basin.

- **NORM** can be a treatment challenge with the settled solids presenting an additional management consideration, especially in the event of a large-scale reuse facility that may generate tons of NORM containing solids. Therefore, while various technologies can be used for NORM removal in produced water, further optimization and analysis is needed in order to more effectively consider management of the NORM in treatment train design. The level of NORM in produced waters varies greatly by geography and formation. NORM should be a primary consideration in the treatment technologies considered.

- **Dissolved organic constituents (DOC)** are ubiquitous in water and have various sources. For produced water, these sources are the natural organic matter found in the makeup water, the organic chemicals present from the fracturing fluid mixture (i.e., friction reducers), organic constituents from the formation (i.e., hydrocarbons), and chemicals that form during subsurface reactions between these three main sources. There are various treatment technologies aimed at removing this DOC, such as activated sludge process or biologically activated filtration, which rely on microorganisms to remove DOC. The TDS levels in produced water present challenges for these microbial based treatments, since elevated levels of TDS are known to impact even the degradation of carbohydrates. Biological treatments have been demonstrated at TDS levels greater than 100,000 mg/L, but these were from other industries (i.e., pickling or tanning wastewater) or synthetic waters, and had long hydraulic retention times (> 100 hrs.). Additionally, produced waters may contain specific organic constituents in

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the DOC, like biocides or phenols that are inhibitory to microorganisms. Membranes, such as ultrafiltration, nanofiltration, and reverse osmosis can also be used for the removal of DOC. However, they will require significant pre-treatment to protect the membranes from fouling and are also impacted by the TDS levels; since TDS levels greater than 50,000 mg/L are typically inhibitory, due to the pressures required and low water recovery levels.

Because treatment system efficacy is highly dependent on the type, concentration, and behavior of DOC, which can be variable in produced waters, and thorough piloting of treatment systems is highly recommended. For example, pH variability during treatment can cause the precipitation of DOC, causing significant fouling of treatment systems. Other treatment technologies, such as thermal distillation, can handle DOC and produce a high-quality distillate however DOC will be concentrated in the blowdown or waste stream from this process unless there is a thermal destruction aspect of the treatment. Technology selection will be dependent and vary by location, as well as residuals management needs; particularly for membrane-based processes.

- **TDS** is the total of organic and inorganic constituents dissolved in a given water. In produced waters TDS is dominated by sodium and chloride, but can include various metals, hardness, and alkalinity to list a few. Many treatment processes do very little for these dissolved solids, which can be the most challenging and expensive constituent to remove in produced water. Removal of TDS is being demonstrated around the globe with seawater desalination, but levels of TDS in produced water are generally higher, with many basins having average TDS content ranging up to several times that of seawater (see Figure 3-13). Technologies aimed at addressing TDS for waters greater than 50,000 mg/L currently include primarily membrane distillation, thermal distillation, and crystallization. The challenges associated with these technologies are many, but primary considerations include associated costs and the need to manage significant amounts of salts and/or concentrated solids that may be contaminated with constituents of concern removed in treatment.

![Figure 3-13: Water Quality by Basin (TDS and Chlorides)](image)

**Source:** 18 Producing Companies (from Module 2, Figure 2-61)

Figures on Y axis represent Mg/L. Many basins have average TDS content ranging up to several times that of seawater.

The challenges and costs involved in the design and use of treatment systems necessary to meet reuse quality objectives are primary considerations in any reuse scenario and must be investigated early in the decision process.

A substantive table reviewing current treatment technologies and known removal of constituent classes is shown in Appendix 3-E.

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Theoretical Treatment Trains
When evaluating treatment technologies, it is critical to understand treatment goals, particularly how technologies are used together in “treatment trains” and the capabilities of these systems. A treatment train is often needed to address the many types of constituents in produced water, and will include multiple steps to remove various constituents, in a strategically designed stepwise fashion. Each step in the treatment train will be considered for its ability to remove the specific constituent or class of constituents and manage its resulting residual solids or sludges, which could be substantial. The treatment train needed for any given reuse scenario could look significantly different from others based on the produced water and the water treatment goals. Each technology has its own pros, cons, and purposes.

Figures 3-14 to 3-17 depict theoretical treatment trains for select produced waters. The authors have included these as theoretical options to illustrate that several steps are needed to treat produced water and that treatment combinations vary depending upon produced water character and quality objectives. Numerous potential combinations are possible and it is likely that additional steps may be required. Although residuals management is not fully considered here (i.e., suspended solids removal), it is a vital component of design.

Figure 3-14: Low-TDS Treatment Train #1 (<40,000 mg/L TDS)
In the first step, coagulation/flocculation removes suspended solids and hardness in the produced water. In the second step, microfiltration removes additional suspended solids and large organic constituents. In the third step, reverse osmosis targets dissolved constituents, both organic and inorganic (i.e., TDS and DOC). In the final step, advanced oxidation targets oxidizable organic constituents.

Figure 3-15: Low-TDS Treatment Train #2 (<40,000 mg/L TDS)
This variation leads with dissolved air flotation to remove suspended solids. The second step is a biologically active filtration step to reduce both suspended solids and dissolved organics. The next step is granular activated carbon to target dissolved organics and some remaining suspended solids. The final step is nanofiltration to address both dissolved organics and total dissolved solids.
Treatment Technology: Research Recommendations

The treatment of produced water presents a unique challenge and opportunity for the oil and gas industry, researchers, and regulators alike. Considerable unknowns regarding the precise chemical character of produced water can impact the design and evaluation of treatment trains for various reuse scenarios. Furthermore, water quality variation from location to location, means that there is no single solution or “silver bullet” for produced water. It is likely that each basin, and perhaps even sub-basins or specific operational practices, will require a thorough investigation on best practices and technologies available for treating their produced water and the outcome of this investigation is likely to change depending on end use.

The following research considerations could be addressed by operating companies, academic institutions, government research groups, or collaborative partnerships. Scenario-specific research and development may include more targeted objectives not mentioned here.

1. Expand data development and publication of the efficacies and capabilities of different treatment scenarios for different produced waters;

2. Conduct desk-top/bench-scale or pilot-scale treatment demonstrations of non-synthetic produced water sampled from a variety of geographies and time scales;
3. Identify strategically engineered treatment trains able to manage removal of constituents of concern to necessary levels while producing manageable residual streams;
4. Conduct realistic, field-scale piloting of individual treatment technologies and treatment trains to assess response to expected changing variables, flow rates, produced water quality, upsets, etc.;
5. Further investigate technologies/methods that can recover valuable resources from produced water that may offset treatment cost;
6. Develop strategies to manage treatment residuals, taking into account waste characterization and disposal, the potential for recycling, reuse or sale, and storage and transportation;
7. Identify indicator constituents or classes of constituents to help assess the treatment of produced water and consider the parallel use of whole effluent analytical methodologies to flag pass-through of constituents of concern; and
8. Expand analysis of factors unrelated to effluent quality outcomes, such as energy requirements, emissions, footprint, and infrastructure.

State of the Science: Literature Review
Research conducted in areas relevant to this module has significantly increased in recent years. GWPC worked with collaborating experts to conduct a literature review with a goal to cast a relatively broad net and gather references and resources that may be useful to this discussion moving forward. For example, the literature review included studies related to “degraded water” reuse, which is the reuse of mostly fresh waters that have been contaminated in some way through their initial use for things like industrial processes, household effluents, or runoff. While these waters may differ from produced water in their character and origin, this subject was included in order to provide a more complete assessment of literature around the concept of treatment and reuse of waters that may be more traditionally considered a waste. Learning from the process and findings of research in this somewhat analogous area can inform produced water reuse assessment, research, and decision-making. Similarly, many of the existing peer-reviewed studies that directly address produced water analyze the produced water prior to treatment or consider chemicals utilized in hydraulic fracturing fluids.

The search logic and process for identification, review, and evaluation of the literature is described with more depth in Appendix 3-F. Rather than simply provide references and citations, the summaries that follow present a cursory overview of the “state of the science” in the four topics covered in the review: (1) degraded water reuse, (2) produced water quality, (3) produced water reuse for non-oil and gas purposes, and (4) environmental and human health hazards and potential risks from produced water reuse. A bibliography organized by topic is available in Appendix 3-G. The following sections provide an overview of each topic and a summary of where, how, and why research was conducted along with generalizations about findings. The overviews do not substantively present the findings of all papers covered by the literature review and does not address other relevant topics or issues of concern such as policy or regulation unless directly relevant to the literature reviewed.

Note to readers: this is only one discrete literature review effort. It does not include all possible papers, subjects, and references that may be relevant to produced water. In fact, informative studies on a variety of topics or reuse scenarios are likely not represented here. Where projects are proposed or proceed, conducting a more targeted literature review may be a useful component of initial assessment of that effort.

Degraded Water Reuse
Background
Rising water supply demands worldwide have contributed to increased interest in the intentional reuse of degraded waters. Degraded water, typically fresh water that has been subjected to chemical, physical, or microbiological degradation, can provide various opportunities through reuse. Research on the use of degraded water has primarily focused on: industrial wastewater effluent; municipal wastewater effluent; graywater (wastewater without fecal contamination); irrigation/livestock runoff; and, stormwater runoff (O’Connor et al. 2008). While the papers covered here are not specific to produced water reuse itself,
the process and concepts considered for reuse of other degraded waters, such as municipal wastewater, can be informative.

Reuse options can be divided into non-potable, indirect potable, and direct potable reuse. Non-potable reuse options include reuse in agriculture (i.e., crop irrigation, livestock watering), industrial (e.g., cooling tower blowdown, road-spreading/dust suppression), and urban reuse (e.g., golf courses, highway medians). Indirect potable reuse of degraded water may include surface water augmentation and groundwater recharge. These “indirect” methods typically involve careful planning with safeguards in place to protect human and ecological receptors and rely on mixing, dilution, biological buffering mechanisms (such as nitrite and ammonia assimilation by plants) or engineered buffers to provide multiple layers of protection in the environment (Metcalf and Eddy 2007, O’Connor et al. 2008). Direct potable reuse (DPR) is similar to indirect potable reuse (IPR), however, unlike IPR there are no environmental barriers in DPR and therefore advanced treatment systems are needed (EPA 2017). As of 2017, Texas and New Mexico were the only states with planned or implemented DPR systems (EPA 2017).

Some effort has been made to aggregate water quality guidelines for reuse, though this work has not been exhaustive. Pham et al. (2011) compiled water reuse guidelines from international sources as a “decision-analysis screening tool” that may be useful to assess reuse for irrigation, livestock, aquaculture, and drinking water. The study identified guideline values for at least one reuse option for over 50 water quality parameters (Pham et al. 2011). While an increasing number of regulatory programs surround non-potable reuse like graywater systems, specific regulations for indirect and direct potable reuse are less common. Some states like California, Arizona, Florida, Oklahoma and Texas have policies or programs that support or encourage various degraded water reuses and, some states are working toward development of programs and regulations for other reuse options. Beyond this high-level overview, specifics of regulatory programs are not commonly included in peer-reviewed literature, a few citations on this point are included here as footnotes. Where an operator, state, municipality or other group is interested in a specific reuse program, investigation of the regulatory systems surrounding various types of degraded water reuse should be conducted in addition to a search of the peer-reviewed literature.

Potential human health risks
Adverse health risks from water reuse can result from both direct and indirect exposure to contaminants. Health risks due to microbial organisms have been addressed the most frequently (Weber et al. 2005) and were the primary human risk factor mentioned in many of the reviewed papers on degraded water reuse (Hamilton et al. 2006; Hamilton et al. 2007; Hyland et al. 2015). Microbial pathogen exposure from contact with human or animals waste could occur when reclaimed water from livestock water or municipal waste water is not effectively treated prior to reuse. When used for irrigation, known contaminants of concern in degraded water may enter the human food chain if they accumulate in edible crops. Potential health risks due to the uptake of emerging chemicals of concern such as pharmaceuticals, endocrine disrupting chemicals or EDCs, and other emerging contaminants of concern (ECOC) have not been as thoroughly addressed and were not routinely discussed in published review papers on water reuse (Bikerton et al. 2011; Anderson et al. 2013). Li et al. (2013) evaluated the occurrence and concentrations of EDCs in aquifers recharged with reclaimed municipal wastewater. Results show that EDC concentrations decreased with greater aquifer depth but increased when reclaimed wastewater was continuously discharged during the dry season. Blaine et al. (2014) found that perfluoroalkyl acids (PFAAs), which are persistent organic contaminants, bioaccumulated in the edible portion of strawberries and lettuce. A recent review by the NRC (2012) suggests that the number of potential chemicals in reclaimed municipal wastewater is in the thousands, indicating that monitoring requirements should be more robust and comprehensive than those used currently.


Potential ecological risks

Ecological risks of degraded water reuse are based on the quality of the water at the time of release. Treated wastewater effluents are regularly discharged into waterbodies via a point-source discharge after undergoing secondary or even tertiary treatment (NRC 2012). Although these discharges are subject to multiple layers of treatment before discharge, and generally involve permits with applicable discharge limits, they may still contain a mixture of organic and inorganic chemicals that may cause unanticipated adverse effects in the receiving environment. Other ecological impacts may include a change in pH, dissolved oxygen, temperature, nutrient loading (phosphorus, nitrogen), and increased total dissolved solids (TDS), and total suspended solids (TSS) (Soucek et al. 2011).

Ecological impacts from non-point source runoff is also a concern when water reuse involves the application of a degraded water to land, such as with crop irrigation. O’Conner et al. (2008) note that approximately 29% of the total volume of irrigation water returns as irrigation return flow. Therefore, any contaminants of concern may leave the application site as run-off and enter surface waters.

Direct application of reused water to land must also account for the potential for increased soil sodicity, or an increase in sodium held by the soil. Some recycled water, high in dissolved salts, may increase the salinity in the soil to levels that are unacceptable by either native vegetation or planted crops. Further, Hyland et al. (2015) suggests water reuse evaluation studies are not effectively evaluating plants as many of these studies have included hydroponic test exposures and therefore, do not account for soil-root/plant interaction. Many additional papers are included in the bibliography, including a large body of agricultural literature on sodium adsorption ratios, etc. that may be useful to consider with respect to produced water.

Understanding risk of degraded water reuse

Degraded water reclamation and reuse research includes reclaimed water from a variety of sources. Several studies emphasized the need to develop a consistent risk assessment framework to evaluate degraded water in the context of potential reuse scenarios, similar to the discussion of produced water in this Module. For example, FitWater, (Chhipi-Shrestha 2017) provides a decision support tool (DST) for evaluating degraded waters in the context of the reuse scenario in question. A final ranking score allows risk managers to then make the best decision regarding reuse options based on several criteria including: the amount of degraded water to be reused, the cost of treatment, potential health risks (based on microbial risk assessment, particularly with surface water reuse scenarios), energy use, and carbon emissions. The ranking/scoring system provides a straightforward conclusion allowing risk managers to either move forward with a specific reuse or treatment option. Chen et al. (2013) proposed a Full Assessment procedure for use in Sydney, Australia to evaluate reuse options based on technical, economic, and social principles to implement a preferred reuse. Although similar in that the tool provides a final score, this tool was unique in that it also included a social impacts evaluation.

The literature included in this review provides useful suggestions for the development DSTs and a risk assessment framework that can be used to implement a method by which water reuse scenarios can be consistently evaluated. However, risk assessment strategies evaluated in these publications do not thoroughly consider potential human health risks or ecological consequences from chemical exposure. One major gap in both human and ecological risk assessments is the mixture toxicity of various chemicals found in wastewater (NRC 2012). Although the toxicity of chemicals with similar modes of action can be predicted using the sum of the toxicity of the individual components (e.g., PAHS, DiToro et al. 2007), it is far more difficult to predict toxicity when modes of action are different (NRC 2012). Further, the long-term impacts from exposure to chemical mixtures is not understood and may require additional testing to validate model predictions. As outlined by the NRC (2012), additional understanding of contaminant attenuation, environmental buffers, and potential chemical transformation and byproducts due to treatment or biological and abiotic interactions are important in the development of appropriate treatment and reuse options. Although this review did not directly assess the impacts of irrigation run-off (irrigation return flow) to human and ecological health, this pathway must be considered when sources of irrigation of water are considered. Research needs such
as this parallel some of the considerations provided in this module and may be relevant to produced water reuse assessment.

**Produced Water Quality**

Produced water is the largest waste stream associated with oil and gas extraction; it has a highly variable composition that can depend upon the geology of the field, the type of hydrocarbon being developed, and the age of the well (Fakhru’l Razi et al. 2009). While the major compounds of produced water are generally consistent, the concentration of the constituents can vary by orders of magnitude (Wesolowski et al. 1987, Igunnu and Chen 2017).

In general, produced water is a complex mixture of inorganic and organic constituents such as dissolved and dispersed petroleum hydrocarbons including polycyclic aromatic hydrocarbons, geogenic minerals associated with the formation including NORM, heavy metals, monovalent/divalent/multivalent elements and salts, and added production and maintenance chemicals and their transformation compounds (Alley et al. 2011, Oetjen et al. 2017, 2018, Hoelzer et al. 2016). According to the USGS Geochemical Database, the total dissolved solids (TDS) of produced water ranges from fresh (less than 500 mg/L) to hypersaline (greater than 500,000 mg/L, Blondes et al. 2017).

**Early studies and federal databases**

In their 1987 report prepared for the Gas Research Institute, Wesolowski et al. note that for produced water, “dTetailed chemical analyses and quantitative summaries of treatment and disposal practices were severely lacking.” That early study sought to increase understanding of produced water by collecting and analyzing seventeen samples of produced water from sixteen natural gas production sites. The team used methods and parameters defined previously in a study conducted by EPA (Wesolowski et al. 1987). A summary of this study as well as data generated by studies conducted by EPA and the American Petroleum Industry (API) can be found in Fillo et al. (1992); however, these studies limited their characterization to conventional water quality parameters, minor and trace metals, volatile and semi-volatile organic compounds, and RCRA criteria.

Currently, two federal sources of data are available on oil and gas wastewater: the U.S. Geological Survey (USGS) National Produced Waters Geochemical Database and the Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drilling Water Resources (US EPA 2016). The USGS Geochemical Database was recently updated (v2.3, 2017) and is currently a compilation of 40 databases, publications, or reports, though it is continually growing (Blondes et al. 2017). While the original database focused on major elements only (e.g., TDS, sodium, calcium, and chloride), the new database has been expanded to include trace elements, isotopic data, and time-series studies of produced water changes. This database includes data from conventional and unconventional oil and gas developments as well as geothermal wells. However, the database is limited with respect to organic compounds. For example, not including geothermal, injection well, or undefined well data, of the 113,374 samples in the database, less than 2% have limited organic chemical data. Furthermore, many entries are missing basic data, such as location (10% lack data), sample date (26% lack data), and the depth of the well or sample (29% lack data). For those that have sample dates, 90% were sampled prior to 2000.

The second database is presented in Appendix H to the Final Report of the EPA’s Assessment on Hydraulic Fracturing on Drinking Water Sources (2016), which reports on the chemicals identified in fracturing fluid, flowback, and produced water, but without any corresponding concentration data. The appendix contains 1,606 chemicals that were reported to be used in hydraulic fracturing fluids or detected in produced water of hydraulically fractured wells. Additionally, this study identified 131 chemicals that have been detected in produced water that do not have an associated CAS number, and therefore were not included in the following analysis. The reported chemicals used downhole are from 2005–2013 and total 1,084 unique compounds; there were 599 chemicals found in literature on oil and gas wastewater, 77 of which were also reported to be in hydraulic fracturing fluid as identified in 28 sources. These sources are listed in the appendix and included both peer-reviewed literature and industry or state-based...
research including the New York State Department of Environmental Conservation (NYSDEC, 2011), Geological Survey of Alabama (2014), the Pennsylvania Department of Environmental Protection (PADEP, 2015), industry self-reporting, and a study conducted for the Marcellus Shale Coalition member companies by the Gas Technology Institute (GTI, Hayes 2009).

However, EPA notes that this database for “… flowback and produced water chemicals identified… is almost certainly incomplete” (Ch 9. EPA, 2016). The EPA indicates that the relatively small number of studies, combined with a lack of comprehensive analytical methodologies, as well as complex matrix interference rendering standard methods inappropriate, have resulted in chemicals being undetected. Importantly, the report concludes that “… standard analytical methods are not adequate for detecting and quantifying the numerous organic chemicals, both naturally occurring and anthropogenic, that are now known to occur in produced water” (Ch 7, EPA 2016).

A third and up-to-date resource is the FracFocus chemical registry that includes disclosures of chemicals used in hydraulic fracturing. This database is publicly available and can be downloaded to evaluate chemical use patterns in specific development areas and may also be useful in identifying potential constituents of concern.

**Non-standard analytical methods (research methods)**

In their assessment of emerging technologies and analytical methods for use in produced water, Oetjen et al. discuss the hurdles in characterizing oil and gas wastewater including the suitability of analytical methods in hypersaline water and the lack of methods for many suspected chemicals in produced water (2017). As another example of analytical challenges, Nelson et al. demonstrate that the complex matrix common to produced water interfered with EPA standard methods to measure NORM, reducing the recovery of radium-226 to 1 percent of its total (2014).

To meet these chemical characterization challenges, method validation along with a combination of target, suspect, and non-targeted analytical methods are needed (Oetjen et al. 2017). To this end, a number of research groups have demonstrated the efficacy of sample preparation techniques to remove or reduce matrix effects combined with non-targeted screening or high-resolution mass spectrometry (HRMS) methods to identify previously unknown compounds in produced water (Hoelzer et al. 2016, Khan et al. 2016, Luek and Gonsior 2017, Luek et al. 2017, 2018, Maguire-Boyle and Barron, 2014, Nell and Helbling 2018, Piotrowski et al. 2018a, 2018b, Rosenblum et al. 2017, Thurman et al. 2014, 2017). Additionally, Thacker et al. developed a number of analytical methods to characterize oil and gas wastewater from West Texas unconventional developments, which they used to identify a number of chemicals that are commonly reported as hydraulic fracturing fluid components, including 2-butoxyethanol, cocamide diethanolamines, and o-xylene (2015).

Hoelzer et al. (2016) analyzed flowback and produced water from six Fayetteville Shale wastewater samples using advanced non-targeted gas chromatographic analytical techniques. The research team were able to identify approximately 400 organic chemicals and attempted to categorize the source of the chemicals as likely geogenic, disclosed production chemicals, or likely anthropogenic. The researchers also identified several suspected transformation products or undisclosed compounds. Those compounds included halogenated compounds, which, due to low disclosure frequency, are likely unintended transformation products. Halogenated organic compounds are concerning due to their likelihood to be persistent organic pollutants.

Thurman et al. identified polyethylene glycol surfactants (PEGs), polypropylene glycol surfactants, and linear alkyl ethoxylates (LAEs) using high-resolution liquid chromatography (2014, 2016). Using the same methodology, Ferrer and Thurman were able to identify and elucidate the chemical structures of the biocides alkyl dimethyl benzyl ammonium chloride (ADBAC) and glutaraldehyde, and cocamidopropyl surfactants (2015). The authors found that ADBAC was present in 54% of samples collected from flowback and produced waters in Weld County, CO.

Khan et al (2016) analyzed produced water from the Permian basin (shale-oil) from eight wells, using non-targeted methods to look for volatile organic compounds. Samples were collected late enough
after production that the researchers surmised that they represented native formation water rather than hydraulic fracturing fluid. They were able to confidently identify 327 compounds; primarily known as being from the source oil.

Despite the recent increase in peer-reviewed literature on novel method development and characterization of produced water, Luek and Gonsior found the majority of samples for these studies are not necessarily collected where most oil and gas are being produced and therefore may not be representative of produced water generally (2017). Approximately 70 percent of the studies to characterize organic compounds from hydraulic fracturing fluids and wastewater were conducted with produced water sampled from the Marcellus basin, which only accounts for 37 percent of natural gas production and less than 0.01 percent of oil production (Luek and Gonsior 2017). However, continued development of these methods and their application to greater and more diverse types of produced water is an important first step towards creating robust, standard methods.

Produced Water Reuse for Non-Oil and Gas Purposes

There have been several proposed or implemented strategies for produced water management that seek to capitalize on its value as a water source, though peer-reviewed literature on these reuse scenarios as-applied have been limited to date. Active or hypothesized reuse options include: aquifer storage and recovery (ASR); subsidence control; mitigating salt-water intrusion; agriculture and irrigation uses; industrial uses, such as in power production or tower cooling; dust suppression and road deicing; salt and/or elemental extraction/recovery; and even as potable drinking water (see, e.g., Veil 2011). Studies that have investigated the impacts from these implementations are not common and instead most often focus on the potential for or treatability of produced water for new purposes (see, e.g., Dallbauman and Sirivedhin 2005; Echchelh, Hess, and Sakrabani 2018; Guerra, Dahm, Dundorf 2011; Hagstrom et al. 2016; Horner, Castle, and Rodgers 2011; Martel-Valles et al. 2016; Oetjen et al. 2018b, Sirivedhin and Dallbauman 2004; Xu, Drewes, and Heil 2008). Most of these studies conclude that while possible in select circumstances, most produced water will require high levels of treatment to meet reuse objectives outside oil and gas operations, which is likely to be currently cost-prohibitive.

Where research exists on irrigation with produced water, it has primarily focused on coal bed methane (CBM) produced water due to its availability and often lower-salinity characteristics. (Beleste et al. 2008; Bern et al. 2013; Burkhardt et al. 2015; Ganjegunte, Vance, and King 2005; Ibrahim, Marroff, and Wafi 2009; Johnston, Vance, and Ganjegunte 2008; Mullins and Hajek 1998). Collectively, these studies indicate that direct application of CBM to soil can have deleterious effects on both the plants and the soil, causing leaf-burn and affecting soil infiltration and its structure. However, careful consideration of the types of soil, how the irrigation is applied (i.e. sub-surface irrigation) (Beleste et al. 2009, Bern et al. 2013), and if the plant is salt-tolerant (Rambeau et al. 2004) have led to some successful use of CBM in the short-term. Long-term application exacerbates harmful effects on soil and is not recommended (Burkhard et al. 2015; Ganjegunte, Vance, and King 2005). Jackson and Meyers examined the feasibility of using CBM in hydroponics and aquaculture by growing tomatoes and cultivating tilapia, respectively (2002). Tomatoes grown with CBM were smaller, tasted salty, and had elevated levels of sodium, chloride, arsenic, barium, chromium, lead, selenium, and silver. Tilapia had a 27% mortality rate when grown in produced water versus the control; however, there was some discrepancy in the counting the total number of fishes grown in the control.

Heberger and Donnelly (2015) compiled a table of nine projects where produced water has been used for crop irrigation in California. Studies are ongoing regarding food-safety and other considerations regarding this practice as specifically applied in the Central Valley. There have been a handful of greenhouse studies that have been conducted on the use of oil and gas produced water for irrigation of tomatoes (Martel-Valles et al. 2014) and non-food crops including western wheatgrass and alfalfa (Brown et al. 2010), hemp and cotton (Rambeau et al. 2004), and biofuels like switchgrass and rapeseed, which are considered relatively salt-tolerant (Pica et al. 2017). Martel-Valles et al. found that two of the three different produced waters could successfully grow tomatoes, however, they found that the plants had a decreased leaf-weight indicating some detrimental effects on biomass (2014). The third produced water...
was unsuccessful, which they attributed to elevated levels of petroleum hydrocarbons, copper, and chloride concentrations, despite having comparable TDS levels to the other waters tested. Brown et al. found that produced water had to be treated prior to use for irrigation, and that the type of treatment affected the elemental compositions uptaken by the plants (2010). Pica et al. looked at a variety of dissolved solids and organic carbon concentrations in produced water and found that high salinity, as well as organic content of produced water reduced biomass production and that five inorganic compounds were uptaken by the plants (2017).

Studies that specifically investigate soil implications are limited. Some studies relevant to land application have considered impacts related to soil application as a form of disposal (Al-Haddabi and Ahmed 2007) or as a result of spills (Oetjen et al. 2018a), though context should be given in translating conclusions from these studies to intentional reuse scenarios where treatment is likely to occur. More recently, some researchers have launched efforts to more fully understand potential impacts of produced water on not just crops but also on soil health. For example, a team at Colorado State in Fort Collins is actively investigating potential impacts of the use of treated and diluted produced water for irrigation of wheat crops and associated effects on plant growth as well as accumulation and leaching processes in agricultural soil.213

Finally, studies also exist regarding road-spreading for various purposes. Currently, thirteen states allow for road-spreading of produced water (Tasker et al. 2018) either for de-icing or dust-suppression, though some studies have indicated that its use is ineffective for dust-control (Graber et al. 2017). Studies of this reuse option have also found that road-spreading contributes to increased radium in roadways (Tasker et al. 2018), and increased metals concentration in the environment around the application site (Graber et al. 2017) and due to leaching after rain events (Tasker et al. 2018).

Environmental and Human Health Hazards and Potential Risks from Produced Water Reuse214

The current state of the “impacts” literature on produced water

Alternative uses of onshore produced water may alleviate one of the predominant waste management issues associated with unconventional and conventional oil and gas production while reintroducing a potentially valuable resource, especially in arid and agricultural regions. However, the risks associated with introducing treated produced water into the environment and resulting environmental, wildlife, and human exposures have not been comprehensively evaluated. This section of the literature review aims to (a) identify scientific reports on environmental and human health impacts of produced water, and (b) define knowledge and gaps in the literature pertaining to chemical contaminants of concern, relevant exposures, and human and environmental health impacts. Details on the scope of this review can be found in Appendix 3-F, which provides an overview of the methodology and search logic. Software-aided evaluation of the search results revealed a strong focus on compositional, exposure and ecotoxicological studies (Figure 3-18 A–D). Currently, approximately equal numbers of articles focus on onshore and offshore produced waters. While offshore produced water is not a part of the Module 3 assessment thus far, literature pertaining to offshore produced water was included in our search. This substantial body of literature is included because produced waters are in many ways expected to be similar in chemical character to produced waters found onshore, recognizing variations that might occur from basin to basin and due to different production practices. Numerous similar concepts can provide insight, such as analytical methodology to quantify contaminants of concern, whole effluent toxicity tests, and the nature of geogenic contaminants associated with hydrocarbon reservoirs. Due to this general similarity, studies of offshore produced water may inform an assessment of onshore produced waters, even though not all information captured may be directly relevant to

213 See, e.g., http://borch.agsci.colostate.edu/group-members/molly-mclaughlin/

214 GWPC would like to thank ExxonMobil Biomedical Sciences, Inc. for their significant contribution to this portion of the literature review summary and their services in assisting to conduct the review itself. Portions of this section have been presented by ExxonMobil Biomedical Sciences, Inc. in a poster session: F.A. Grimm, K.P. Christensen, K.S. Lavelle, S.I. Maberti, M.S. Alexander, T.F. Parkerton, D.J. Devlin, “Review of Environmental and Human Health Hazards from Alternative Applications of Produced Water,” Poster Presented at the National Academies of Science Workshop on Strategies and Tools for Conducting Systematic Reviews of Mechanistic Data to Support Chemical Assessments, December 10-12, 2018, Washington, DC.
onshore produced water management. Additionally, more historical information and data are available on offshore produced water management due to different operational realities and regulatory requirements for management, including discharge. For these reasons, the summary below does not, in every case, explicitly identify a study as onshore or offshore, however the cited papers reviewed for this section can be referenced for detail if necessary. Furthermore, temporal publication trends reveal a proportionally much stronger recent increase in the onshore literature compared to stagnant numbers of articles investigating primarily offshore produced water (Figure 3-18 A). Consistent with increasing interest in alternative applications for onshore produced water produced water, there is a rising number of publications related to agricultural uses, treatment and remediation, biomarker discovery to track exposures, and human health impacts in recent years.

Potential risks from produced water with special emphasis on hydraulic fracturing

Risk perception of produced water effluents is linked to compositional concerns and biological evidence derived from environmental and human health related toxicological studies. Produced waters are complex mixtures comprising a wide array of naturally occurring and man-made chemicals, predominantly salts, hydrocarbons (e.g., mono and polyaromatic compounds) and low molecular weight acids, but also potentially harmful contaminants including metals and radioactive materials (Figure 3-18 B–C). Recent evidence indicates that conditions during unconventional oil and gas operations can be favorable for catalysis or halogenation of aromatic constituents. Environmental concerns thus stem from both salinity and xenobiotic exposures to harmful contaminants. Laboratory and field studies provide further evidence for harmful properties of produced water, reporting adverse effects on various marine, aquatic and terrestrial organisms, including acute and chronic toxicity, mutagenic, developmental and reproductive effects, and potential for endocrine disruption. Comparably few studies have specifically addressed human health concerns of produced water. In most cases, excess lifetime cancer risk was estimated to be negligible, but non-cancer health risks appear to warrant further evaluation due to limited exposure data particularly for metals.

Most of the peer-reviewed literature focuses on assessing effects of untreated produced water and/or individual, often concentrated, chemical fractions of produced water. As treatment and remediation procedures, for example by desalination, electro-oxidation, and photo (electro) catalysis, continue to improve the quality of produced water streams, these treatments will likely reduce associated toxicities, e.g., mutagenicity, by removing associated constituents of concern from the produced water.
Figure 3-18: Software-Assisted Literature Evaluation and Trend Analysis

Search hits were analyzed in Sciome Workbench for Interactive Computer-Facilitated Text-mining (SWIFT). (A) Total number of search hits associated with major search categories; (B) Number of search results for major classes of chemical constituents of produced water; (C) Heatmap representation of temporal and chemical constituent-based publication trends; (D) Search term frequency-based fingerprint of all relevant search results; (E) Search term-recognition based publication hits related to endocrine-disrupting chemicals. [Abbreviations: T=title, A=abstract, EDC=endocrine disrupting chemical, VOC=volatile organic compound]
Constituents related to produced water
Produced waters are often high in total dissolved solids (TDS) and halides (e.g., chloride, bromide, fluoride), and may contain metals (antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, mercury, molybdenum, nickel, selenium, silver, strontium, thallium, vanadium, zinc, uranium and thorium), and NORMs such as $^{226}\text{Ra}$ and $^{228}\text{Ra}$ (Figure 1B) (Birkle et al. 2005, Mofarrah et al. 2011, Lampe et al. 2015, Bzowski et al. 2015, Chittick et al. 2017, Luek et al. 2017). The concentration of individual constituents can be highly variable and depends on the geologic characteristics of the formation (Bou-Rabee et al. 2009, Bzowski et al. 2015). Produced water that contains flowback water from hydraulic fracturing operations may contain a variety of chemicals that comprise fracturing fluids (Table 3-3).

Produced waters may also contain a wide range of concentrations of volatile and semi organic compounds (VOCs and SVOCs) that originate from contact with the crude oil/gas or are introduced by drilling fluids. Among the most common VOCs are BTEX (benzene, ethyl-benzene, toluene, and all xylenes), mixed alkanes, and naphthalene (Luck et al. 2017). Similarly, a wide variety of aromatic compounds including alkylated benzenes, alkylated naphthalene’s, PAHs, phenanthrenes, phenols, and pyrene have been reported in a number of studies characterizing produced water (Chittick et al. 2015, Luck et al. 2017). Several gases such as methane, hydrogen sulfide, and carbon oxides can be found dissolved in produced water and can be released into ambient air. Fracking fluids include a mixture of a wide variety of non-petrogenic substances, including acids, biocides, corrosion inhibitors, pH control agents, and gellants (Table 3-3).

Last, a combination of physical, chemical and biologically mediated reactions may transform fracking fluid or geogenic substances. A number of small organic acids are produced through microbial transformation under the anaerobic conditions; acetates are a byproduct of the degradation of organic additives; and halogenated organic compounds can be formed when hydrocarbons are in contact with halogenated salts or biocides suggesting that halide salts or free halogens are created during oxidative treatments can cause the observed halogenation (Luck, 2017). Other disinfection by-products can be formed during the treatment of produced waters, especially those with high contents of chlorides, bromides, or other halides.
Table 3-3: Summary of the Types of Chemicals Commonly Used in Hydraulic Fracturing

<table>
<thead>
<tr>
<th>Type</th>
<th>Function</th>
<th>Selected Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>Improve injection or penetration; dissolve minerals</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>Biocides</td>
<td>Prevent bacterial growth, which can erode pipes</td>
<td>Glutaraldehyde; Quaternary ammonium compounds; Tetrakis hydroxymethyl phosphonium sulfate</td>
</tr>
<tr>
<td>Breakers</td>
<td>Break down of gellants; added to enhance flowback</td>
<td>Ammonium persulfate; Sodium, calcium chloride; Magnesium oxide; Magnesium peroxide</td>
</tr>
<tr>
<td>Clay stabilizers</td>
<td>Prevent clay plugs of fractures</td>
<td>Choline chloride; Sodium chloride; Tetramethyl ammonium chloride</td>
</tr>
<tr>
<td>Corrosion inhibitors</td>
<td>Reduce rusting</td>
<td>Isopropanol; Methanol; Formic acid; Acetaldehyde</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>Maintain fluid viscosity; may include carrier fluids</td>
<td>Potassium metaborate; Triethanolamine zirconate; Petroleum distillate; Boric acid; Zirconium; Sodium tetraborate</td>
</tr>
<tr>
<td>Friction reducers</td>
<td>Enhance efficiency of fluid movement</td>
<td>Polycrylamide; Methanol; Ethylene glycol; Petroleum distillate</td>
</tr>
<tr>
<td>Gellants</td>
<td>Increase viscosity and suspend sand during proppant transport</td>
<td>Guar gum; Polysaccharide blend; Ethylene glycol; Hydrotreated light petroleum distillate</td>
</tr>
<tr>
<td>Iron control</td>
<td>Prevent precipitation of metal oxides</td>
<td>Citric acid; Acetic acid; Thioglycolic acid; Sodium erythorbate</td>
</tr>
<tr>
<td>Non-emulsifier</td>
<td>Prevent formation of emulsions, and as a product stabilizer</td>
<td>Lauryl sulfate; Isopropanol; Ethylene glycol</td>
</tr>
<tr>
<td>pH control</td>
<td>Maximize effectiveness of other additives</td>
<td>Sodium hydroxide; Potassium hydroxide; Acetic acid; Sodium carbonate</td>
</tr>
<tr>
<td>Proppants</td>
<td>Hold fissures open for gas &amp; oil escape</td>
<td>Silica (quartz; sand)</td>
</tr>
<tr>
<td>Scale control</td>
<td>Prevent mineral buildup and clogs</td>
<td>Copolymer of acrylamide and sodium acrylate; Sodium polycarboxylate; Phosphonic acid salt</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Decrease surface tension and improve fluid passage</td>
<td>Lauryl sulfate; Ethanol; Naphthalene; Methanol; Isopropyl alcohol; 2-butoxyethanol</td>
</tr>
</tbody>
</table>

* Adapted from FracFocus, [https://fracfocus.org/chemical-use/what-chemicals-are-used](https://fracfocus.org/chemical-use/what-chemicals-are-used).
Assessments identifying endocrine disrupting chemicals

Endocrine disruption is a term describing complex chemical interactions with endocrine systems in living organisms, which can lead to adverse outcomes including developmental effects and carcinogenicity. Certain PAHs, alkylated PAHs, alkylphenols (AP), naphthol’s, and naphthenic acids (NA) have been linked to endocrine-disrupting effects in marine biota, and the presence of these and other chemicals with potential endocrine disrupting potential (Figure 3-18 E) in produced water has raised awareness, especially with respect to fresh and salt water environments. APs have emerged as chemicals of primary concern with currently 52 unique structures being confirmed in produced water streams from nine different locations in the North Sea and Norwegian Sea (Boitsov et al. 2007).

In addition to the presence of chemicals of concern, evidence exists from laboratory studies supporting endocrine disrupting potential of untreated produced water or its individual constituents in fish and in vitro models. Estrogen (ER) and androgen receptor (AR) activities are indicative of potential for progression of certain breast and prostate cancers in humans and are among the best studied endocrine phenotypes. At the molecular level, produced water exposure has been correlated with increases in plasma concentrations of the estrogenic activity marker vitallogenin (Geraudie et al. 2014; Sundt et al. 2011). Corroborating evidence for these observations stems from in vitro estrogen receptor assays demonstrating the presence of ER active constituents and androgen receptor AR activity in vitro. However, consistent with geological variation, results varied significantly across multiple produced water samples, including samples without associated endocrine activity. Thomas et al. (2009) evaluated individual fractions of produced water samples, concluding that short-chain APs and naphthenic acid contribute approximately 35% and 65% of the ER agonist activity. Knag et al. (2013) observed AR activities in freshwater fish treated with commercial mixtures of NAs. Altogether, these studies demonstrate that petrogenic constituents are major contributors to produced water-associated ER/AR activities. Knag et al. (2013) also reported estradiol and progesterone induction and inhibition of testosterone production in human H295R cells exposed to APs, NAs, and the polar fraction of produced water. At the organism level, exposure of zebrafish embryos to high concentrations of isolated organic fractions of produced water resulted in developmental effects included spinal malformations, hatch delay, and pericardial edema (He et al. 2018).

Evidence-generating studies

As noted in the introduction to part 1 of this section, the scope of this review was broad enough to gather information from a wide variety of sources deemed informative in some way to assessing produced water, its chemical characterization, and potential impacts from its release or reuse. Some papers include offshore produced water analysis, while others focus on analyzing the constituents used in operations and potentially present in produced water, untreated produced water, and even spill impacts. In all cases, where data exists to better understand produced water there presents an opportunity to gather information that can inform more targeted assessments such as prioritizing chemicals for analytical method development or focusing research objectives for a particular reuse scenario.

Exposure considerations

Occupational exposures to the salts and radioactive materials can occur during handling and deposition of the precipitate or filtration cakes, handling of the solids, or resuspension of the material during transport and/or after deposited. The present literature review did not identify studies specifically addressing these concerns.

When considering surface application for dust abatement, irrigation of crops, or livestock water supply, there is potential for the accumulation of metals, salts, and NORM in the soil matrix. Occupational and non-occupational exposures can occur due to contact with contaminated soil, indirect soil ingestion, or ingestion of crops irrigated with these waters. Several studies on produced water spills to soil report that NORM and metals tend to be sorbed onto nearby soil and not transported far from the spill location (Birkle et al. 2005), but do not address the potential direct or indirect exposure to contaminated soils through ingestion, inhalation, or contact or mechanical dispersion from tires or dust. At least one study has evaluated the potential risks of contact with contaminated soils, reporting potential non-cancer endpoints.
Human exposure can result from consumption of contaminated food that has been in contact with produced water contaminants (Mofarrah et al. 2011, Werner et al. 2015); but the significance of these pathways has not been reported in the literature.

Most of the air quality concerns addressed in the literature are concerned with venting, fugitive gas emissions and diesel emissions during operations. No studies were identified that evaluated potential air exposures during beneficial reuse of produced water. Similar to emissions during operations, storage of produced water in open air pits, aeration, or dispersion of produced water may lead to the emission of volatile organic compounds such as BTEX, CO, H2S, NOx and even particulate matter (including crystalline silica and heavy or rare metals) (Lampe et al. 2015, Chitick et al. 2017). These emissions will mainly lead to occupational exposures but may also impact air quality in nearby communities.

**Human health**

The human health literature consists largely of theoretical attempts to conduct health hazard/risk assessments for spill scenarios, with most studies focusing on quantifying cancer risk, although some examine both cancer and non-cancer endpoints. Overall, the literature is characterized by variation in the target population (occupational, residential), exposure scenarios (swimming in a contaminated pond, use of contaminated reservoir for residential drinking water supply), exposure route (inhalation, dermal, oral) and assumptions (length of exposure, time to event, dilution rate) and model choice (deterministic, fuzzy rule-based, Monte Carlo). Some exposure scenarios consider operations that may no longer be practiced in certain regions (e.g., open-air storage of flow back water) and therefore may not be relevant to an assessment of a particular application or reuse scenario. Given the dates of publication for most of the papers, this appears to be a growing area of study (Figure 3-18 B).

Results of the identified body of literature are challenging to summarize given the differences across studies and dearth of total studies. The health effects literature reveals mixed results and should be interpreted with caution. Although some studies report excess lifetime cancer risks (among the general population) between $10^{-10}$ to $10^{-6}$ under various dermal, inhalation and ingestion scenarios due to radionuclide exposure (Abualfaraj et al. 2018; Rish et al. 2018; Torres et al. 2018), other studies that evaluated cancer risk related to radioactive materials exposure (Shakhawat et al. 2006) or exposure to polycyclic aromatic hydrocarbons (Chowdhury et al. 2009) observed no significant increases in cancer risk.

Non-cancer hazard index has also been examined in risk assessments of produced water, with similarly mixed results. Barium and thallium were associated with increased risk for non-cancer outcomes (Abualfaraj et al. 2018), whereas in an assessment of non-cancer outcomes due to metals exposure, risk was reported to be well within acceptable limits (Mofarrah et al. 2011).

Worker health has also been considered in the produced water literature. In a study that examined health risks of inhalation exposure to 12 volatile organic compounds (VOC) present in flow back water, Bloomdahl et al. (2014) did not observe an increased risk of adverse health effects due to any of the VOC measured, whether modeled as hazard quotients, hazard indices or excess lifetime cancer risk. In an assessment of cancer risk due to dermal exposure among workers, Durant et al. (2016) observed few substances (benzo(a)pyrene, heptachlor, and barium) related to excess cancer risk i.e. exceeding $10^{-6}$.

**Ecological receptors**

- **Freshwater life.** Fracturing fluids and onshore produced water (which may contain flowback containing residual substances used in fracturing fluids, maintenance and production, as well as transformation products) have been characterized with regard to mostly freshwater aquatic wildlife, typically stream-dwelling fish and invertebrates. Effect levels are highly dependent on the produced water type and the associated hydrocarbon formation, i.e., oil, gas, or coalbed methane (CBM), also referred to as coalbed natural gas, coal seam gas.

  Among the contaminants exerting the greatest ecotoxicity concern in fresh waters, dissolved salts (TDS comprised primarily of major ions Na+, Ca++, Mg++, K+, Cl-, SO42-, HCO3-) are the most abundant and due to their high solubility in water, they can exert a strong influence on species distribution. In dried
salts or reject brines from treating produced water from conventional and shale operations, metals and NORM are concentrated, elevating the potential hazards of the salts. TDS consisting mostly of NaCl can be over 250,000 mg/l in some shale gas produced waters, e.g., from the Marcellus and Bakken formations. Additional minerals arising from produced water whose effects on freshwater aquatic life have been measured include barium (Golding et al. 2018), iron and manganese (Duarte et al. 2018).

Freshwater organisms are sensitive to TDS over a range of concentrations beginning at less than 1,000 mg/l, based on conductivity (a generic reflection of saltiness; Cormier et al. 2013). CBM produced water (CBMPW) comes from shallow formations and tends to be brackish rather than briny, and less laden with associated metals and petroleum hydrocarbons than produced water from unconventional production and may be suited for discharge to streams after minimal treatment (USGS 2000). Farag and Harper (2014) evaluated toxicity of sodium bicarbonate in CBM simulated waters to develop a species sensitivity distribution of common laboratory and receiving stream (Powder River, Wyoming) species, concluding inhibitory concentrations between 500-1000 mg/l may be exceeded in undiluted produced water.

Organic contaminants from the formation and also from fracturing fluid are present in some produced water and exert toxicity to freshwater organisms (Butovskyi et al. 2017) including PAHs (He et al. 2017), alkylpenols (Holth et al. 2008) and quaternary amine compounds. Organism responses evaluated range from invertebrate survival and growth (Blewett et al. 2017) to swimming proficiency, cardiotoxicity, respirometry, transcriptomics and biomarkers in zebrafish (Danio rerio) (Folkerts et al. 2017; Holth et al. 2008), providing a range of response endpoints as dilutions of produced water constituents.

- Marine life. Effects of produced waters on marine organisms have been well-studied, concomitant with a lengthy history of off-shore produced water discharges (Figure 1B). Offshore produced water discharges rely on dilution by seawater and movement by ocean currents to limit exposure of marine organisms to produced water contaminants. Ecotoxicity screening of many produced waters from platforms, discharge sampling points, and the edges of mixing zones demonstrates that while undiluted marine produced water is typically toxic, it is diluted to below organism-effect levels within a short distance of the discharge point. Nevertheless, the body of literature regarding marine species details methods and findings that may be transferable to land-based discharge options.

In the past two to three decades increasing interest has been focused on biomarkers of exposure of cod (Gadus morhua) in the North Sea, where fish migratory grounds intersect a high number of platforms. These include effects on acetylcholinesterase (ACHE, neurotransmitter), oxidative stress proteins, and DNA damage, among a broad number of molecular tools (Hasselberg et al. 2004, Sturve et al. 2006, Holth et al. 2010, 2011a, 2012). There is some indication of broad-reaching presence of produced-water induced biomarkers in the North Sea (Balk et al. 2011). As noted by Holth (2010), the biomarkers need to be tied to physiological effects in order to be incorporated into risk assessments. Additionally, it has been observed biomarker up-regulation early in exposure often gives way to compensatory pressures as organisms acclimate to new conditions, which complicate use of biomarkers in decision-making (Abrahamson et al. 2008).

Studies using marine mussels are generally focused on bioaccumulation of produced water contaminants, primarily PAH parent and alkyl-substituted congeners (Brooks et al. 2011). PAH fingerprinting indicates in many settings the mussels are exposed to both petrogenic and pyrogenic sources, though the source of pyrogenic emissions is uncertain. Solid-phase extraction of PAH from seawater
provides similar to slightly-higher results, indicating biomimetic extraction using passive sampling could be used instead of mussel (or oyster) tissue monitoring (Durell et al. 2006; Harman et al. 2011).

- **Livestock.** A limited number of studies considered livestock watering as a potential beneficial use of produced water (Horner et al. 2011) or coalbed natural gas produced waters (Jackson and Reddy, 2007a; Zhang and Qin, 2018), with only Horner et al. (2011) specifically conducting a series of conceptual risk evaluations to assess the aggregate risk of the various produced water chemicals in several livestock species, including drinking water and dietary intake exposure pathways.

- **Agriculture and soil biota.** Irrigation of crops and soil, or spillage to soil, risks impairing soil function by decreasing water permeation. Direct effects of irrigation water on sensitive crops may also occur. Non-food crops are often preferred for irrigation reuse in order to avoid direct ingestion pathways. Sunflowers (DaCosta et al. 2015, Sousa et al. 2017), castor beans (deMeneses et al. 2017), switchgrass and wormwood (Artemisia) (Burkhardt et al. 2015a, 2015b), and switchgrass and rapeseed (Pica et al. 2017) were exposed to untreated and treated produced waters with a wide variety of results related to product quality and yield, though most indicate at least short-term use with either processed produced water or untreated CBM produced water is acceptable in terms of plant performance, and soil: water ionic interactions. Reverse-osmosis (RO) treatment is not always beneficial to crops. Ferreira et al. (2015a) characterized soil mesofauna and found the produced water that had undergone RO had significant effects on species composition, richness and abundance. Sousa et al. 2016 examined the sunflowers grown in that study and found differences in mineral sequestration with filtered and treated (RO), favoring RO.

**Effects of remediation and treatment**

Among the potential reuse options for produced water, often after treatment, are surface water discharge, livestock watering, irrigation (crop and/or non-food), aquaculture, industrial applications, and dust abatement in roads (Long et al. 2015, Chittick, 2017). In a general sense, water quality for irrigation should be sufficient to 1) protect human health when consuming food produced from crops irrigated with reclaimed wastewater; 2) minimize soil contamination through metal and salt loading; and 3) prevent crop growth inhibition or quality degradation. Bioaccumulation should also be considered. Livestock watering guideline values should be sufficiently stringent to minimize health risks to livestock to ensure successful production. These requirements determine the degree of produced water treatment prior to beneficial reuse.

Produced water treatment in publicly owned treatment works (POTWs) for discharge into receiving streams may impair biological treatment processes, accumulate contaminants in sewage sludge, or facilitate the formation of harmful disinfection byproducts (Chittick, 2017). This is primarily due to the treatment processes at POTWs not being designed to treat this type of water. As a result, unconventional produced waters are no longer permitted to be discharged directly to POTWS in the US, though conventional discharges and indirect discharges from centralized waste treatment facilities are allowed. Produced water evaporation in large, open pits allows for oil and grease to be skimmed off the surface while the remaining water is moved to one or more other pits for evaporation or further management. Potential exposure to air emissions associated with this practice should be considered, as air measurements have reported VOCs (particularly benzene) levels above EPA screening levels (Chittick, 2017). A similar process is the solar evaporation or distillation and crystallization of the produced water. In addition to the potential exposure to air emission of VOCs with this process, of consideration is the potentially large volumes of waste that has concentrated heavy and rare earth metals in these residues that must be disposed or otherwise managed (e.g., potential for recycling/reuse or further extractions for sales in certain circumstances).

Constructed wetland treatment systems used for targeted treatment of produced waters demonstrably enhance characteristics of produced water. Alley et al. 2014 found that various hydrocarbon and metal
markers decreased in excess of 99% and 98%, providing the required efficiency to alleviate ecotoxicity to Ceriodaphnia and fathead minnows. Toxicity of oil sands produced water also decreased, along with metals concentrations, in a hybrid constructed wetland capable of both oxidizing and reducing conditions (Hendrikse et al. 2018).

Other options for produced water treatment include the membrane filtration and reverse osmosis, among others (see the Technology section of this Module). These processes tend to be energy intensive and may not feasible for produced water with high TDS or contamination with gelling agents. Biodegradation of produced water constituents of concern using microorganisms or crops is being tested with different degrees of success, with the salinity of the produced water being a major factor in success of the tests. By contrast, chemical degradation of contaminants using electro-oxidation or photo(electro)catalysis has been reported to provide an effective means to greatly reduce mutagenic activity associated with concentrated organic fractions of produced water samples, thereby indicating the possibility to alleviate this hazard (Li et al. 2006; Li et al. 2007).

Knowledge gap analysis
The following sections highlight uncertainties and knowledge gaps represented by studies that were reviewed as well as highlight research needs that may be associated with those identified gaps.

Analysis of chemical constituents of toxicological concern
Advances in analytical capabilities have improved routine characterizations of produced water composition. However, inherent complexity and variability of produced water due to geologic origin, additives, and decomposition byproducts affects the efficiency of treatment processes, estimates of exposures to constituents of concern, and hazardous properties. Chen et al. (2017) concluded that both uncertainty in existing data as well as a lack of exposure data have prevented risk assessments to move beyond modeling based on spill scenarios. Since beneficial use of produced water outside oil and gas operations is relatively limited compared to internal recycling and deep well injection, very few studies have evaluated the potential for chronic exposures due to direct or indirect exposure pathways that may be involved with reuse.

Endocrine disruption
Current knowledge on endocrine disrupting potential of constituents of produced water is mostly limited to few selected endpoints, particularly estrogen (ER) and androgen receptor (AR) activities, in fish or in vitro.

Field studies
Current risk assessments are predominantly based on spill scenarios of untreated produced water, thereby limiting their utility in appropriate evaluation on environmental and human health risks of produced water in specific reuse scenarios.

Evidence-generating studies involving receptor exposures
- **Human health.** Heterogeneity across studies/assessments greatly limit comparability between different study results and our understanding of potential adverse health effects due to produced water exposure. The primary limitation of the existing literature stems from the uncertainty related to exposure and hypothesized pathways that could theoretically pose an increased risk for adverse outcomes. As the literature currently stands, each risk assessment represents a unique case study of a particular exposure scenario, the relevance of which is not known, complicating the interpretation of the results.

- **Ecological receptors.** Terrestrial receptors may also be impacted by exposure to produced water contaminants — in particular, those species occupying the riparian zone of streams where higher exposures of produced water discharges or runoff could occur — birds, reptiles and amphibians, small mammals, and invertebrates particularly insects, as well as plant life. Within fresh water bodies, there appears to be a dearth of information regarding species sensitivity ranges, as many tests have been conducted using standardized species (e.g., daphnids, fathead minnows, or zebrafish) with only limited studies involving freshwater mollusks including rare/threatened/endangered freshwater mussels; aquatic insects and other arthropods; aquatic plants; and native fish inhabiting the water column or benthos.