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Estimating Recovery by Quantifying Mobile Oil and Geochemically Allocating Production in Source Rock Reservoirs

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Abstract

Due to highly variable well performance, unconventional reservoir (UR) field development relies heavily on production monitoring to predict total recovery, assess well interference, delineate drained rock volume, and diagnose mechanical issues. Completion design and well spacing decisions depend on accurate recovery estimates from reservoir models, and these can be limited by non-uniqueness in the history matching. Geochemical production allocation can greatly improve operators' understanding of well performance when integrated with reservoir characterization and in-reservoir P/T monitoring.

There are several long-standing challenges in the characterization of UR fluid flow: (i) collecting reservoir samples representative of mobile oil, (ii) accounting for production fractionation over the life of a well, and (iii) determining recoverable original oil in place (OOIP) from contributing zones. Although many metrics and correlations are commonly used, ultimate recovery requires accurate quantification of the provenance of produced fluids and proportion of total OOIP.

We have developed a rapid method for quantifying mobile and total oil saturations from water-based mud (WBM) collected, tight cuttings and sidewall core samples using low temperature hydrous pyrolysis (EZ-LTHP). These mobile oils commonly include even the gasoline range compounds, which are the dominant compounds of produced liquids in most mid-continent UR fields, making EZ-LTHP-derived oils representative end-members for geochemical production allocation studies.

EUR estimates and production forecasts by zone, are more accurate when calibrated to the *mobile* oil fraction, rather than to total oil saturation. EZ-LTHP provides this step-change by quantifying the mobile oil fraction in WBM cuttings and, when paired with reservoir volumetrics, allows for better reservoir model calibration and field management. Other industry techniques, such as solvent extraction and vaporization, suffer from the same limitations as log-derived values which are known to *overestimate* mobile oil in kerogen-rich intervals by incorrectly including kerogen-bound immobile oil.

In this paper, we present quantified mobile oil recovery estimates based on integrated geochemical allocation studies from the Vaca Muerta, Neuquén basin, and the Niobrara, Denver basin. In the Vaca Muerta play (Argentina), the organic-rich Cocina and Organico intervals in the Vaca Muerta expelled liquid into intervening good quality reservoir lithologies. However, liquids dominantly are produced from the most organic-rich zones, with evidence of a larger drained rock volume (DRV) during early production. Gas and oil allocations show different DRVs explained by fluid mobility.

The Montney play (Canada) shows contribution of liquid from non-target zones. Interbedded zones of indigenous Montney oil mixed with migrated more mature fluid – and major discontinuities in mud gas isotopes – document minimal vertical mixing. Horizontal wells produce gas and oil dominantly from better-quality reservoirs regardless of landing zone, with natural gas bypassing low permeability zones. Accurate estimations of out-of-zone contributions therefore require cuttings/core-based geochemical allocation. A subset of these wells requires additional consideration of production fractionation.

Introduction

Operators in unconventional reservoir plays need to accurately predict estimated ultimate recovery (EUR) and decline curves to optimize production and economically manage field development. However, highly variable well performance is common in these plays; therefore, field development has evolved to rely heavily on production monitoring. There are a multitude of geological and operational variables that control hydraulically stimulated horizontal well performance. Integration of such variables is essential to predict total recovery, assess well interference, delineate drained rock volume, and diagnose mechanical issues.

All produced petroleum of a lateral at any time represents the commingled MOST mobile fluid flowing at the rate defined by a combination of the fluid viscosity and the effective permeability distribution of the connected reservoir. Predicting the mobile portion of the liquids (effectively % ultimate recovery) ahead of completions is very challenging. For field development, completion design and well spacing decisions depend on accurate recovery estimates from reservoir models and can be limited by non-uniqueness in the history matching.

In unconventional tight reservoir and source rock plays, geochemical production monitoring and allocation has become a common place method for constraining reservoir models (e.g., Albrecht et al., 2022), assessing well interference, and delineating drained rock volume (Jweda et al., 2017). Geochemical production monitoring has been used to diagnose mechanical issues in both conventional and unconventional wells for more than thirty years (Kaufman et al., 1990). Allocation of produced liquids using geochemical fingerprints from core/cuttings samples is a proven technology, used in most fields to refine completion design, well spacing, and field management (e.g., Kornacki et al., 2017). Integration of geochemical production allocation results with reservoir characterization, downhole pressure monitoring, microseismic, fiber optic, and PVT data can greatly improve operators' understanding of well performance.

During depletion drive production, the more mobile components of petroleum are preferentially produced. This phenomenon is particularly apparent in low-permeability reservoirs with high TOC (Han et al., 2018; Song et al., 2022). Accurate allocation of commingled production from contributing horizons benefits from the integration of subsurface data: reservoir quality information, organofacies and mud gas composition, and geochemical data from core/cuttings extracts and from the produced petroleum fluids. In parallel, migrated gas zone identification and produced gas allocation can be derived from mud gas chemistry. Fluid mobility and percent recovery can be estimated by integrating the measured volumes of “mobile” oil-in-place with effective permeability (fluid saturations and permeability) at in-situ conditions. Decline curves and EUR estimates for each contributing zone can then be predicted by applying this approach on time-lapse produced fluid samples from the same well(s) with metered GOR.

In this paper, we demonstrate the preferred methods and generalized workflow to geochemically determine the source of produced hydrocarbon fluids, quantify mobile oil, estimate EOR recoverable reserves, and extrapolate decline target zone curves to arrive at EURs.

Theory and Methods

Production allocation is a non-disruptive method of assessing fluid mobility in the reservoir by comparing the abundances of natural tracers in produced fluids (preferably over time) with the abundances of those same tracers in single-zone end-members from the reservoir. Hydrocarbon (HC) fingerprinting technology can be used to estimate the amount of each kind of gas and oil or condensate that is present in the commingled fluid using C isotope and/or High-Resolution Gas Chromatography (HRGC) data measured on the separator samples and on suitable end-members (Kaufman et al., 1987, 1990; McCaffrey et al., 1996, 2011).

In tight UR reservoirs, this method relies on identifying fingerprints of geochemical flow units based on either produced legacy well oils or liquid extraction from pre-production reservoir samples. The challenge for UR production allocation is finding representative fingerprints of liquid end-members from initial reservoir conditions which (i) correlate quantitatively to the produced fluid (referred to here as “mobile oil”) and (ii) have sufficient vertical discrimination across a reservoir to delineate effective drained rock height. The difficulty in finding such fingerprints is primarily due to the fact that viable tight rock extraction methods (thermal, solvent) poorly emulate the physics of production and therefore do not account for the inherent molecular fractionation that occurs during production (Hartman, 2021).

Geochemical production allocation is commonly accomplished as follows (**Table 1**):

1. Legacy well (> ca. 2 years on production) produced fluids (Pseudo end-members oils) from each of the nearby landing zones are used as end-members to allocate newer wells from similar landing zones. This approach assumes that the legacy wells are producing exclusively from their landing zone, i.e., the drained rock volume has ‘decayed’ back to a small zone around the well (~50 vertical ft).
2. Conventional or rotary sidewall core extracts proximal to produced oil samples from unconventional reservoirs are used as end-members. This option is best if oil-based mud is used, and the goal is to delineate the vertical extent of the drained-rock volume (DRV) and/or the produced fluids for allocation are in an area where no legacy wells are present. Here solvent-extracted oil from core samples obtained from unconventional reservoirs can be used as the end-members (Jweda et al., 2017; Kornacki et al., 2017). The inherent assumptions and limitations of core extract allocations are described below.
3. Wet cuttings extracts are used as end-members if collected in water-based drilling mud. Typically, cuttings are collected at dense sampling intervals (i.e., 10-15ft) for thermal or solvent extraction.

Each of these methods is more suited for different drilling operations and UR plays. Pseudo-end-member oils are easy to collect, do not show the “fractionation” effect of rock-based extracts, and are always readily available except in new appraisal areas where well coverage is limited or plays with a single landing zone. However, production allocation using pseudo-end-member oils cannot delineate DRV extent, or determine the amount of oil coming from non-landing zone reservoirs, as these samples do not exist. The evolution of the DRV (based on longer time-lapse geochemistry studies) and the presence of well interference can be quantified (especially for infill wells). There is a risk that these end-members contain unquantified amounts of the non-landing zone oils, making them prone to underestimating well interference.

Rock samples (accurately georeferenced) across the vertical extent of strata that envelope the DRV of each and all target intervals are needed to delineate the DRV at the sub-target zone level. Core extract end-members from center-cut core plugs work well in areas where oil-based mud is employed; however, core from reservoirs with fluids of API gravity > 43°API must be carefully preserved. This type of work has been challenged by the high expense of core acquisition and the difficulties of using solvent extraction methods to obtain representative rock extracts for end-members for production allocation. Wet cuttings extract end-members are an alternative, since such cuttings are commonly collected vertically through a section of reservoir and are easy to store. However, such cuttings cannot be used if the interval was drilled with a diesel-based mud, as the diesel chemical signature precludes detailed characterization of the native petroleum. To reduce costs, some operators collect cuttings only in the build section, thereby ignoring contribution from below the deepest landed well. Similarly, it is prohibitively expensive to collect

conventional core over thick sections of stacked pay, and rotary side wall cores (RSWCs) are typically of limited quantity and yield poor quality geochemical fingerprints due to rapid oil evaporation (Zumberge et al., 2022).

In these types of fields, identification of oil-generating (kerogen-rich) zones, migrated oil reservoirs, (i.e., containing more oil than the associated kerogen could have generated), and ‘barren’ zones (kerogen-poor, very tight, low oil-saturation intervals) is critical to selecting valid end-members. The geochemical organofacies of each rock extract must be carefully identified to identify true end-members and the significance of the contribution of each zone to the production well streams. If geochemical variations exist at levels thinner than the 10-15 ft sampling interval of cuttings, then the cuttings extracts will consist of mixtures of oil from different organo-facies. Allocation works best using pure end-members; therefore, we typically characterize the geochemical facies using source rock data (Rock-Eval and Leco TOC) along with wireline log interpretation and MICP data.

Although WBM-drilled cuttings are the industry standard for this work, some uncertainty in the exact provenance of cuttings is unavoidable. Even with the best calibrated logging, a given sample will contain some contribution from the overlying horizon, simply due to the mechanics of solid suspension in laminar flow (Clark and Bickham, 1994; Chien, 1992). There is an unavoidable “depth smear” (i.e., progressive vertical separation) of particles en route from the drill-bit to the shaker due to the natural distribution of cuttings size, density, and sphericity (according to the original sediment distribution), and the velocity profile of the mud, which in turn depends on the flow rate and annulus size. The longer the lag time to the shaker table, the greater the separation. Assuming a mud system with constant viscosity and flow rate, the spread of the cuttings increases with depth of bit.

An avoidable but unpredictable challenge is the presence of lost circulation material (LCM) in the mud system. Although this category of additives is common in operations, the timing and quantity are often unreported. Of the many LCM in use, Gilsonite and similar products are the most problematic, due to their similarity to kerogen, and their presence causes the cuttings to appear to have a higher TOC than is representative. Ground walnut shells, cotton seed hulls and similar biological additives, and graphitic carbon are more easily identified as contaminants, but residual oil from their manufacturing can impact results.

Using reservoir rock solvent extracts for production allocation is challenged because extracts contain all extractable organic matter (EOM) from a core plug representative of the initial conditions in the reservoir (nominally C_8 to C_{45+} , or C_{10+} or C_{12+} if evaporated) while produced oil contains a well-mixed average of the mobile oil from the DRV (nominally mobile C_6 to C_{20+} compounds) at the time of sampling. The produced oil compositions will be weighted toward reservoir fluid mobility (rock permeability/oil viscosity), whereas the core extracts will represent the initial composition of *all* oil in all pores of the core plug irrespective of fluid mobility. Removal of the solvents can also remove some of the more volatile compounds, skewing the fingerprint to the heavier compounds.

Quantification of producible oil saturations and production allocation from low-permeability zones in unconventional and conventional reservoirs are long-standing challenges for the industry. Stratum Reservoir has developed a novel method for production allocation of produced liquids from tight reservoirs. The low temperature hydrous pyrolysis (EZ-LTHP) uses scaled-down reactors suitable for wet cuttings materials to produce viable alternatives for end-member oils (Adams et al. 2022). Typically, an aliquot of wet cuttings is rinsed to remove drilling mud solids then loaded into a customized reactor vessel and heated for 12-24 hours. After the head-space gas in the reactor is slowly vented, the reactor is opened, and the mobilized oil is immediately taken to the HRGC where a direct injection method is applied to undertake the fingerprint analysis. The EZ-LTHP oils have been found to be superior to corresponding solvent extracts (CS_2 or Soxhlet) in production allocation projects because their molecular fingerprints are more analogous to produced oil samples. EZ-LTHP for mobilizing oil from wet water-based mud (WBM) cuttings and sidewall core samples enables (Ruble et al., 2023):

- (1) generation of representative end-member HRGC oil fingerprints with a full envelope of light n-alkanes (C₇₊) suitable for production allocation studies, even in wet gas reservoirs,
- (2) quantification of mobile and total oil saturations in unconventional resource plays, and
- (3) analysis of light hydrocarbons that would have been lost via other methods.

In these fields, source rock data, wireline log interpretations, MICP data, molecular and isotopic composition of mud gases and molecular chemistry of rock extracts provide the geochemical baseline of initial reservoir conditions. Preserving volatile HC compounds (especially in wet gas and bubble-point oil plays) present in rock extracts enables identification of end-member fluids by using HRGC data to classify produced/extracted HC liquids using multiple independent methods. *n*-alkane slope factor analysis and estimates of excess methane also elucidate the origin of complex produced fluids. **Table 1** summarizes the development values and applications of the respective end-member types.

Table 1. Applications and suitability of different end-member types to geochemical production allocation studies.

End-member Type	Pseudo End-member Oils	Core Extracts	Cuttings Extracts (WBM only)	Mud gas GC and isotopes
Fluid Type	Any liquid petroleum	Black oils to rich wet gas condensates	Up to lean gas condensate	Wet to lean gas
Pay Zones	Need stacked pay zones	Better for thinner pay zones for complete core coverage	Target zones thinner than 40 ft are a challenge	Rarely works in pay zones less than 50 ft thick
Field Maturity	Minimum single multi-layer pad	Early appraisal and step out into new areas	Early appraisal through infill drilling	Early appraisal through infill drilling
Applications	• Time lapse variations • Well interference • Infill well studies • Qualitative production monitoring	• Drained rock volume with full zonal core coverage • Production allocation of liquids • Well interference • % recovery estimates	• Drained rock volume with full zonal core coverage • Production allocation of liquids • Well interference • % recovery estimates	• Optimum well spacing • Production forecasts and EURs • Model tuning • Inexpensive collection
Field Development Value	• Optimum well spacing • Inexpensive collection	• Optimum well spacing • Integration of petro-physical models • High confidence of sample provenance • Production forecasts and EURs for liquids • Model tuning	• Time lapse variations • Well interference • Production allocation of gas • Reservoir connectivity	• Optimum well spacing • Production forecasts and EURs • Model tuning • Inexpensive collection

Results

In unconventional tight reservoir and source rock plays, allocation of produced liquids using geochemical fingerprints from core/cuttings samples is a proven technology, used in most fields to refine completion design, well spacing, and field management. The spectrum of tight unconventional reservoir types, the range of petroleum system histories, and the variety of reservoir rock sample types result in a variety of best practices for geochemical production allocation (Jweda et al., 2017; Kornacki et al., 2017; Barrie et al., 2020; Lui et al., 2020; Han et al., 2022, and others). As reservoir pressure drops during production, produced liquids and gas become complex transient mixtures of the most mobile petroleum flowing from different reservoir subzones in these tight systems. Here we review three examples of rock-based end-member production allocation in tight unconventional reservoirs: (i) a classic source rock play (Vaca Muerta) with allocations based on solvent-extracted, OBM-drilled core, (ii) a migrated oil, tight reservoir play (Montney) with allocations based on WBM-cuttings extracted with CS₂, and (iii) a system with

naturally fractured, interbedded tight reservoirs with source rocks (Niobrara) with allocations based on WBM-cuttings extracted with EZ-LTHP for mobile oil estimates.

Study 1: A Classic Source Rock Play in the Vaca Muerta

The Vaca Muerta (VM) Formation is the main source rock of the Neuquén basin in Argentina and has been the focus of extensive unconventional resource development recently (Fasola et al., 2023). The operator elected early in their development to execute geochemical production allocation based on core extracts to delineate the effective drained rock height and refine well spacing and completion design for the major landing zones (Fasola et al., 2022). Using time-lapse produced oil geochemistry for wells landed in the three main target zones (Organico Superior, Organico Inferior and the deepest source rock, the Cocina), the produced oils and solvent extracts of 27 core plugs taken over 150 m of the VM were fingerprinted and end-members selected for production allocation. Geochemical extract fingerprints showed clear differentiation between the two major kerogen-rich members (Organico and Cocina) with oil from both source rocks found in the intervening kerogen-poor Regressivo zone. The horizontal wells in this study showed that the wells produced dominantly from their landing zone with some preferential fracture growth correlative to geomechanical characteristics of each reservoir. In particular, the Organico Inferior showed substantial production (~80%) from the overlying Organico Medio during early production but oil fingerprints after 10 months of production suggest that the drained rock volume shrunk back to the landing zone (Fasola et al., 2022).

Integration of reservoir quality, organofacies and mud gas composition with geochemical data from core/cuttings extracts and produced fluids (gas and HC liquids) is essential to accurately allocate the commingled produced fluids. For two VM pads in the oil-producing portion of the play, Fasola et al. (2023) describe how these geochemical allocation results can be leveraged by integration with anthropogenic tracers, core-extract based production allocation of oils, pressure monitoring, and production testing.

Using geochemical markers sensitive to depositional environment, other studies in the oil shale region of the VM show minor facies variations. However, for those studies, the production allocation results based on core solvent-extracted end-members show similar well performance to those reported by Fasola et al. (2023), i.e., dominant production from the landing zone with 15-25% contribution from migrated oil reservoirs (reservoirs with lower kerogen content) above or below the rich source rock zones. To date, core is collected for these studies to minimize the oil-based mud contamination, because water-based mud drilling in the VM is not common.

Development of the VM play is moving into its mature phase, with 100s of time lapse produced oils having been collected in many fields over the last 5 years for geochemical fingerprinting. As observed in the Eagle Ford (Jweda et al., 2017; Kornacki, 2023), Wolfcamp, Delaware basin (Adams and Kornacki, 2022) and Midland basin (Prosser et al., 2020), Pristane/Phytane (a depositional-environment-sensitive ratio) paired with the C_7 expulsion temperature ratio or other C_7 source and maturity parameters clearly differentiate the oils produced from each major landing zone. The same is true for oils from the Cocina landing zone (deeper portion of the VM), which can be distinguished from oils from the overlying Organico member (internal database, Fasola et al., 2023, Han et al., 2022).

This large database of geochemical fingerprints also indicates that wells produce predominantly from their intended landing zone. Time-lapse geochemical production allocation in the VM over the whole field corroborate this finding and show an increase in the production from the wells' landing zones with progressive production. There is more evidence of production fractionation (preferential production of light ends with oil OR production of only a saturated flashed vapor phase) in higher maturity reservoirs, which may be closer to bubble point at the onset of production, therefore expediting two-phase flow and preferential production of gas and light end hydrocarbons (HC). As is the case in more mature fields, simple yet differentiating geochemical ratios can be used for on-going production monitoring (Liu et al., 2020) to identify out-of-zone production in new infill wells or new appraisal areas. Further refinement of drained rock volume would require analysis of cuttings or core extracts as described above.

Study 2: Tight Migrated Oil in the Montney

The Montney play of the Alberta Basin is characteristically very tight with zones of higher permeability reservoir, which provide economic rates of production over more than 30 m on average. These fields are understood to be self-sourced containing high maturity liquids ($>1.2\%$ Ro), typically rich wet to lean gas condensates. Both pressure and gas chemistry discontinuities within vertical section suggest very poor mixing of reservoir fluids. Geochemical evaluation of mud gases in many vertical profiles through the Montney shows high maturity liquids with increasing $\delta^{13}\text{C}$ signatures of wet gas isotopes with depth. There are local excursions of higher maturity liquids roughly coincident with higher permeability zones (**Figure 1 left**) attributed to up-dip migration and dilution of in-situ generated gas (e.g., Laycock et al., 2021; Euzen et al., 2023), but these can be found both just below the Doig Phosphate or deeper in the Middle to Lower Montney. However, the origin of the gas and gasoline range compounds in the produced condensates from the Montney varies over short distances.

Montney operators are still challenged by well spacing and optimal completion design, due to the difficulty in allocating production. It is accepted that gas produced from Montney laterals may be sourced from larger drained rock volumes than are the liquids. All Montney wells exhibit onset of production fractionation, shortly after flowback, which progresses quickly. In-situ fluid mobility distributions are complicated due to charges of different HC fluids into the same reservoir and bimodal pore throat size distributions.

Because the target intervals in the Montney are relatively thin with significant fluid chemistry heterogeneity at the meter-scale, geochemical delineation of DRVs using WBM cuttings extracts collected every 5-10 m is greatly bolstered by collection of mud gas samples for molecular and isotopic composition. Despite the smearing in the cuttings, true fluid end-members, i.e., migrated dry gas, migrated wet gas, and the original petroleum in each zone, can best be identified by integration of poro-perm and MICP data with the geochemical fingerprints, source rock data, and mud gas compositions (Adams and Kornacki, 2019). In more detail, in zones where lean wet gas is found in high permeability rocks, by the time the samples reach the lab the liquid geochemical fingerprint is greatly compromised; Due to pore size, commonly the following is observed: (i) very tight reservoir rock contains only migrated HMG, (ii) good reservoir rock contains migrated fluid with variable HMG, (iii) Tight source rock contains self-generated fluid with minor or no HMG, (iv) high permeability zones with residual HMG, due to evaporative loss. However, the composition of HMG in tighter rocks can be established from those extracts and attributed to the more permeable zones as well.

Here we present a case study from a Montney field, where updip fluid migration and basin uplift have impacted reservoir fluids. HRGC chemistry of CS_2 extracts was used to identify flow unit end-members for allocation of produced oils paired with an integrated mud gas and produced gas allocation study for wells drilled in three target zones on the same pad. Slope factor analysis (Holba et al., 2014), C_7 maturity parameters (Kornacki, 2023), mud gas/produced gas C isotopic data were used to determine the origin of the complex fluid chemistries. **Figure 1 (left)** shows mud gas while drilling data with a gas charge into the Upper Montney of higher thermal maturity wet gas (HMG) characterized by more positive $\delta^{13}\text{C}\text{-C}_2$ and $\delta^{13}\text{C}\text{-C}_1$, associated with a substantial increase in the proportion of C_1 (high C_1/C_2). There is a second lesser discontinuity in the Lower Middle Montney based on the C_1/C_2 ratios which might indicate a dry gas incursion. Geochemical extract fingerprints and C_{15+} molar slope data fit with the mud gas chemistry indicating interbedded zones of mixed indigenous oil with some migrated wet gas, stringers of migrated wet gas including the quasi-conventional Upper Montney reservoir.

Production allocation results using HRGC oil compounds $\text{C}_{10}\text{-C}_{19}$ and mud gas molecular and isotopic composition of C_1 to C_3 for the well landed in the upper part of the Lower Middle Montney (Zone 2) are shown in **Figure 1 (right)**. The higher permeability Zone 1 (located just above the Lower Montney) contains the highest proportion of HMG in the lower part of the Montney section and more kerogen-rich tighter Zone 2 contains the most original oil. Initially, a greater proportion of gas than oil is produced from Zone 2, whereas later in the production history very little Zone 2 gas is produced, i.e., only the solution gas from the Zone 2 oil (Adams and Kornacki, 2019). The Zone 2 contributions of oil and gas after early

flowback do track together; however, obviously Zone 1 contains more mobile petroleum, and it may have reached its saturation point faster than Zone 2. Therefore Zone 1 would yield a greater volume of gas.

Allocation of produced fluids from other wells on the pad identified a high maturity dry gas that made up 20-30% of produced gas coming from the lower Montney, which was not observed higher in the section (Adams and Kornacki, 2019). The proportions of gas and oil coming from each end member zone were roughly consistent if the high maturity dry gas was “removed”, suggesting that this highly mobile gas (95% methane) might be found in stringers or very tight rock (as predicted by Chevrot et al., 2022).

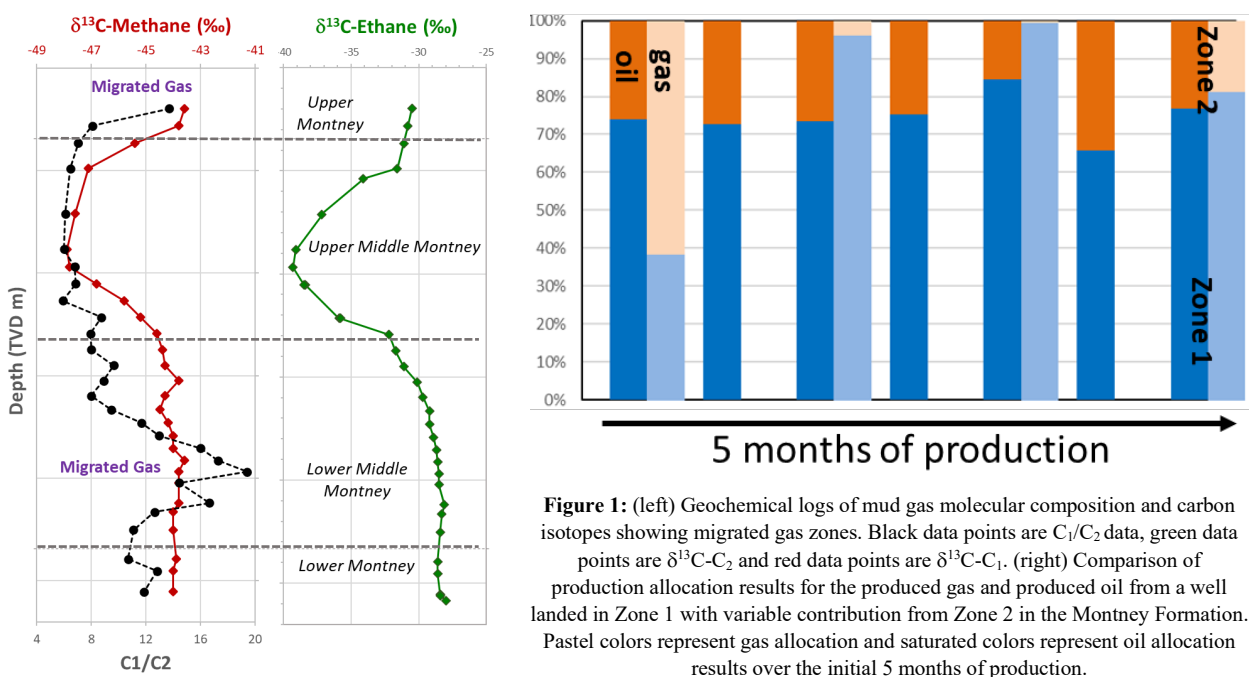


Figure 1: (left) Geochemical logs of mud gas molecular composition and carbon isotopes showing migrated gas zones. Black data points are C_1/C_2 data, green data points are $\delta^{13}\text{C-C}_2$ and red data points are $\delta^{13}\text{C-C}_1$. (right) Comparison of production allocation results for the produced gas and produced oil from a well landed in Zone 1 with variable contribution from Zone 2 in the Montney Formation. Pastel colors represent gas allocation and saturated colors represent oil allocation results over the initial 5 months of production.

Only through integration of poro-perm data with mud gas data, HRGC geochemistry and source rock data could the produced oil and gas chemistry and sample alteration be accurately understood. This pad used different completions to assess their impact on which zones contributed to the production stream. Additional understanding of variability in reservoir quality away from the pilot well would assist in predicting produced fluid properties and CGR over time more accurately.

Study 3: Mobile Oil Quantification from Niobrara Cuttings

In this study, 23 water-based mud drilled, wet cuttings from the Wattenberg Field in Colorado were collected through the unconventional Niobrara targets and into the Codell Formation. The reservoirs in this part of the field are exemplified by dense natural fracture systems and large faults through the target reservoirs of the A Marl, B Chalk/B Marl, C Chalk and the Codell Formation. Due to the structural complexity of the reservoirs and well trajectories, the new EZ-LTHP application was implemented to quantify “mobile oil” and “total oil” saturations using as-received, post-LTHP and post-Soxhlet TOC and SRA (Source Rock Analyzer) data (**Figure 2 top right**). The sequentially extracted samples for the main target zones were also measured by NMR to get an independent measurement of “mobile oil” and “total oil”. Additionally, the HRGC fingerprints on these wet cuttings were used for production allocation of 16 oil samples collected June 2022 from 4 wells landed in each target zone.

Simple source and maturity parameters from the HRGC data showed increasing Pristane/Phytane and increasing light-end HC maturity with depth in the oils and mobilized cuttings extracts. We used HRGC peak-height ratios to classify the samples using Hierarchical Cluster Analysis (HCA) results, and to identify

end-members and mixing lines between the commingled samples using Principal Components Analysis (PCA) results (Kornacki et al., 2019). Commingled samples subsequently were allocated using over 100 non-evaporated and non-fractionated HRGC peak heights.

Figure 2 (left) shows the variation in TOC and scaled production index as a measure of reservoir zones (where the two logs diverge) versus kerogen-rich (source rock) zones where the two logs converge. These organofacies classifications do not always correlate to the lithostratigraphy, i.e., reservoir in the chalks and source rock zones in the marls. We typically use these designations to ensure that end-members of each organofacies from each stratigraphic zone are included in an allocation study.

Interestingly, the TOC, which is commonly used as a proxy for source rock reservoir richness, does not positively correlate to the EZ-LTHP-derived mobile oil (producible EUR volumes by depletion drive alone) and total oil ([S1+S2 as received] – [S1+S2 post Soxhlet]). Quantification of mobile oil and total oil (**Figure 2 right**) shows that Niobrara extracts have substantially more total oil and mobile oil than do the conventional Codell reservoirs, which contain almost the same amount of mobile oil as total oil (close to 1:1 ratio). The Niobrara rocks, however, have much lower Mobile/Total ratios suggesting substantial amounts of sorbed oil that could be recovered by EOR (EOR Oil: additional producible EUR volumes, i.e., oil not bound to kerogen, and not mobile by depletion drive alone).

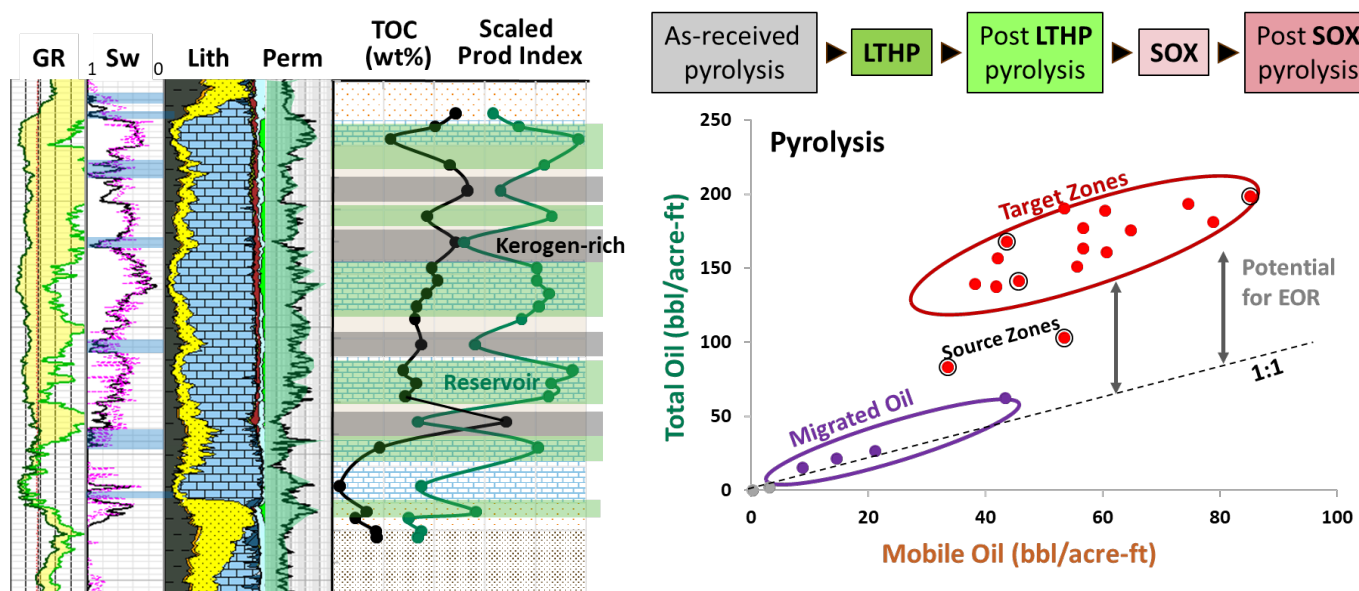


Figure 2: (left) Geophysical logs for gamma ray, water saturation, lithology and permeability (log scale) are compared to the measured TOC (wt%) and scaled production index ($S1/(S1+S2)$) to determine organofacies as predominantly “reservoir” zones in green (where the production index is high, and TOC is low) or “kerogen-rich” source rock zones in gray (where the two logs cross are or are close). (right) Total vs. Mobile oil (bbl/acre-ft) for all 23 cuttings samples. The best source rock samples are identified by a black outline; Niobrara/Sharon Spring cuttings are in red, and Codell cuttings are in purple.

NMR wireline log data are commonly collected to establish mobile fluid volumes as part of a standard package of geophysical logs. Lab NMR (12 MHz) core analysis is a non-invasive, powerful, and reliable tool with 100 times higher resolution than wireline 2MHz NMR to accurately determine porosity, pore size distribution, fluids saturation, and permeability. Pore size is proportional to NMR relaxation time, i.e., small pores have smaller T2 times, and large pores have larger T2 values. Using this model, lab NMR T1 and T2 relaxation times are used to differentiate oil, brine, and kerogen volumes, which are indistinguishable to the wireline unit.

For this Niobrara cuttings study, NMR analyses were performed on each cuttings sample both “as-received” and after each sequential extraction so as to monitor the progressive removal of liquid oil. NMR detected a decrease in the pore fluid volume post-EZ-LTHP and a peak shift to faster relaxation times associated

with lower fluid volume in the same pore space (**Figure 3**). The post-LTHP oil is assumed to be sorbed on to the kerogen or too heavy to move under extraction conditions. With sequential extraction, NMR oil volume decreases for each sample (**Figure 4**), with there being substantially more mobilized oil during solvent extraction than during EZ-LTHP extraction. NMR estimates of oil volume in the three main contributing zones to produced oil in these wells (**Figure 4, right**) agree within 10% to Total Oil as measured with the EZ-LTHP data, with even closer agreement in the marls. The lack of systematic differences between the two methods indicates comparable results.

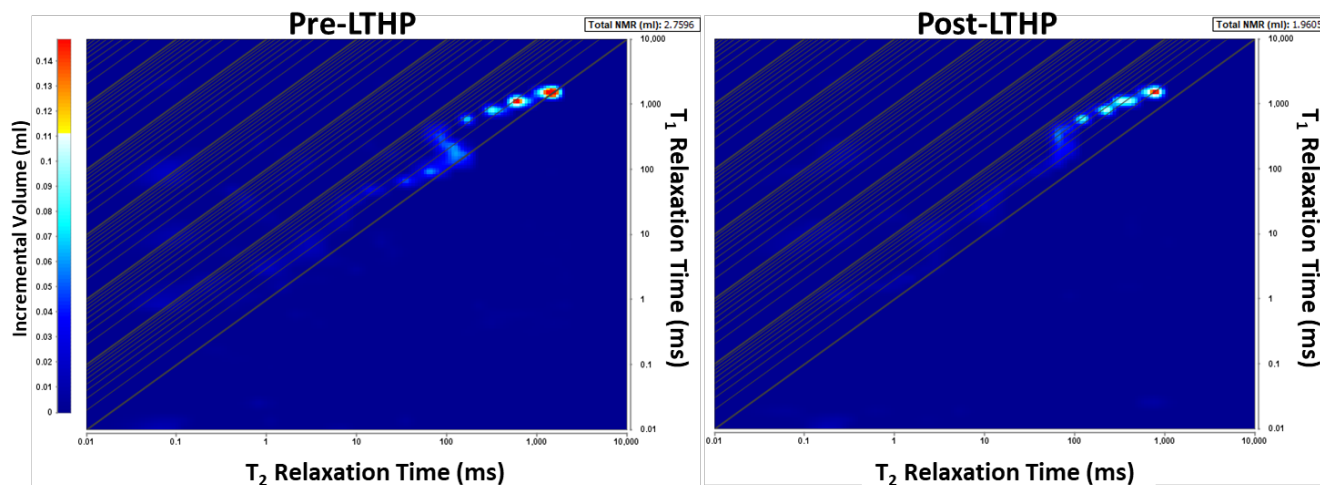


Figure 3. T1-T2 maps were collected both pre-LTHP (left) and post-LTHP (right) testing and reprocessed above. NMR detected a decrease in the pore fluid volume post-LTHP and a peak shift to faster times associated with lower fluid volume in the same pore space.

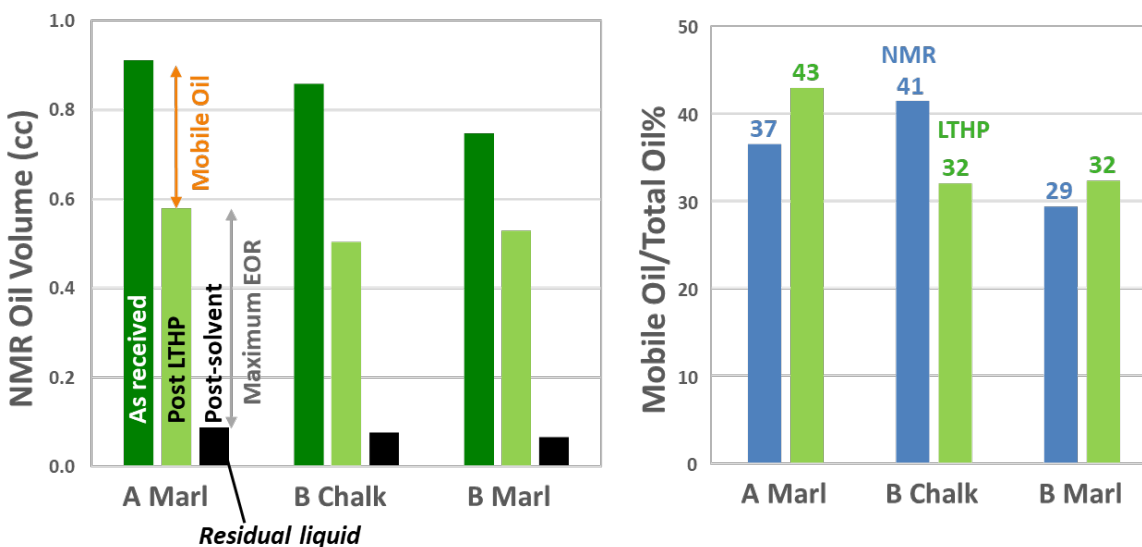


Figure 4: (left) NMR reported oil volume in cm^3 for three cuttings samples contributing the most liquid to the produced oil from this pad, which were measured as-received, after LTHP extraction and after Soxhlet extraction (post-solvent). Residual liquid is most likely water (right). Mobile/total oil in percent as estimated by NMR in blue and LTHP in green for three cuttings samples.

Sections of this profile where mobile oil and permeability are high and water saturation low (**Figure 5**) are considered good candidates for depletion-drive production. Where mobile oil is approximately equivalent to total oil, e.g., in the Codell Formation, there is ostensibly no EOR potential unless primary production is relatively inefficient. In this example, only 25-35% of the mobile oil is being produced leaving substantial mobile oil in the reservoirs for re-stimulation or miscible-flood EOR to recover (thin orange mobile oil line in **Figure 5**). Therefore, in this case, re-stimulation may greatly enhance production in the Codell. This shows that measuring mobile oil by this method could be used to identify zones which might yield substantially more oil via re-fracs, prior to Huff and Puff or chemical EOR is attempted.

The measured ratio of mobile to total oil (**Figure 5, Log Supplement**) can be used to correct petrophysical logs with more accuracy than can a simple scalar from the NMR log correlated back to lithostratigraphy. Areas where the EOR oil is high has the best potential for tertiary recovery (**Figure 5, Development Decisions**).

For geochemical production allocation, 12 end-members were identified as being statistically distinct (out of the 23 cuttings EZ-LTHP mobilized oils). For those 12 samples, there was at least 3% difference in the heights of the HTGC peaks selected from C₁₁-C₁₆. The Codell cuttings samples exhibited too much evaporation and drilling mud alteration to be used with the other cuttings extracts for allocation. Instead, an alternative method would have to be implemented in this dataset to determine the proportion of Codell oil produced from Niobrara landed wells (e.g., Han et al., 2022; Dolan et al., 2022).

Here, 12 of the 16 oils were allocated using quantitative unmixing methods McCaffrey et al. (2011); however, a novel method to capture the contributions and uncertainty of the solutions using all 12 end-members was used. **Figure 5** shows the contribution from each zone to the produced liquids normalized to 100% from a horizontal well landed at the base of the B Chalk (“Reported”), with the 85% confidence range in the reported contributions.

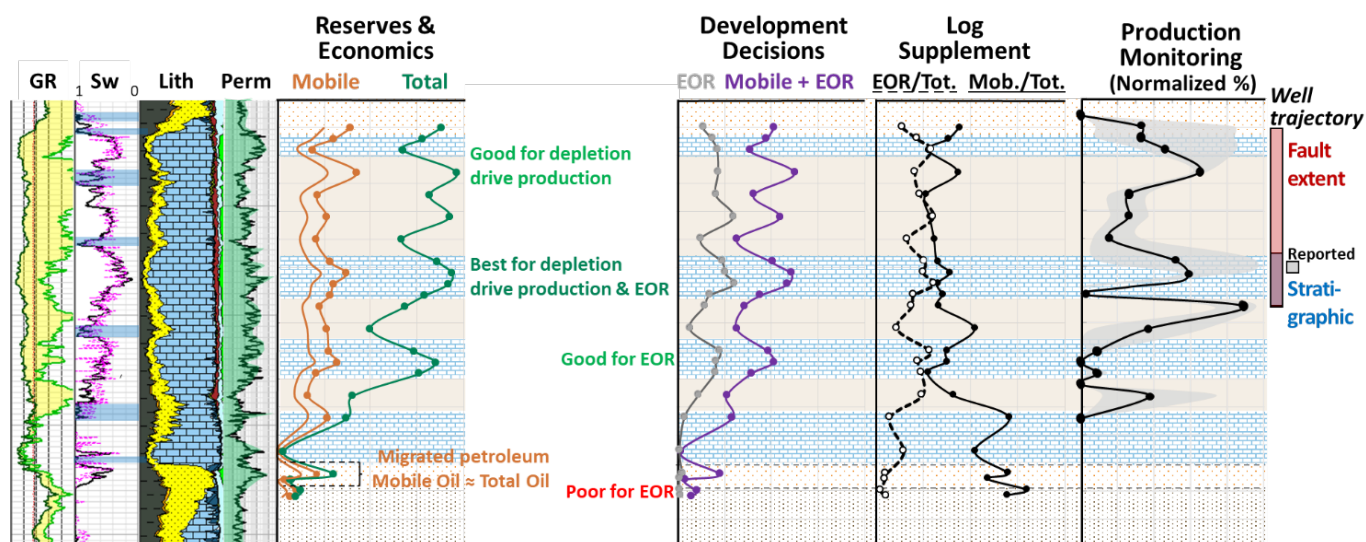


Figure 5: Series of geochemical logs: Mobile oil and total oil determined from SRA analyses, with the solid orange line representing a hypothetical mobile oil related to production inefficiency. EOR oil is the additional producible EUR volumes (oil not bound to kerogen, and not mobile by depletion drive alone). Log Supplement curves show ratios that could be applied to logs to more accurately report mobile oil and EOR potential. Production monitoring log is the contribution from each zone to the produced liquids normalized to 100% from a horizontal well landed in the B Chalk (“Reported”). Gray shading indicates the 85% confidence range in the reported contributions. The well trajectory (**Figure 6**) extends across the shaded zone labeled Stratigraphic, and, due to faults, the well intersects strata across the “Fault extent” section.

For this B Chalk landed well, most of the produced oil is derived from the landing zone and the underlying B Marl, with non-contributing zones in the B Chalk and C Chalk possibly related to local facies or compromised cuttings samples. Also, there is more contribution from the upper A Marl and A Chalk than expected. A Marl landed wells do not have any appreciable contribution from the C Marl and allocations of Niobrara C landed wells have greater uncertainty due to its limited number of viable cuttings samples and its tight nature/high kerogen content of the C Marl. Furthermore, the allocation results for all the wells landed in the A Marl and C Chalk show some contribution from their landing zone, but also substantial contribution from the B Marl, an unanticipated high level of commingling.

Figure 6 shows the structural complexity of these reservoirs, with >50 ft of throw on major faults, and the toe up well trajectory in the example B Chalk-B Marl well. Some of the other wells in this study cut through two large faults and have greater trajectory tortuosity than in **Figure 6**. This high level of contribution from outside many of the landing zones is attributed to natural fractures connecting thicker vertical sections.

Some end-members associated with slightly lower permeability zones and/or higher water saturation zones consistently do not contribute much to the produced oil. These results reflect fluid mobility in a natural fracture-dominated system enhanced by hydraulic simulation, such that even small unfavorable changes in relative permeability related to in-situ petroleum viscosity, oil saturation or permeability will minimize production from that part of the reservoir.

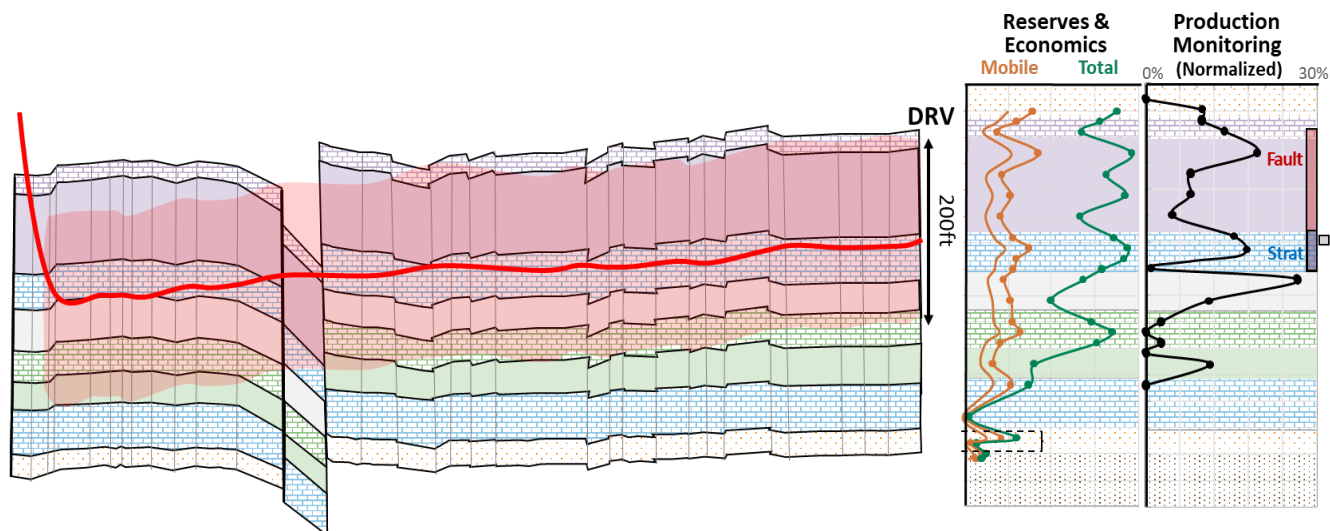


Figure 6. Cross-section showing the B marl-B Chalk landed well trajectory (red line), with hypothetical 100 ft and 200 ft drained rock height in shaded red. Production allocation results for this well are shown with stratigraphic extent of the well trajectory shown on the left as in **Figure 5**.

All reservoir rock-based allocations assume lateral homogeneity in end-member geochemical fingerprints. In this case, it is likely that over geological time migration of oil and compositional equilibration occurred along the natural fractures, thereby creating local variability in fluid composition not found in more typical layer cake stratigraphic plays. **Figure 6** shows that even a conservative 200 ft drained rock height given the well trajectory would easily have contribution from the C Marl to the A Chalk if the fault zones are considered. This may explain why the prolific B Chalk-B Marl zone is such a major contributor to all the production wells in these pads. Here, we conclude that the substantial commingling observed in produced fluids can be attributed to well trajectories crossing multiple stratigraphic zones due to faulting; and hydraulic fractures tying into and enhancing the natural fracture system.

Predicting well performance and well interactions using natural tracers in this type of a play is challenging. There was some minor well interaction identified from a Niobrara B well contributing a Niobrara A landed well. Time series samples and integration of production data (as in **Figure 7**) are required to assess well interactions with more accuracy and assess well performance.

Discussion

Geochemical production allocation in classic source rock plays like the Eagle Ford, Vaca Muerta, and Bakken (Jweda et al, 2017; Kornacki et al., 2017; Long et al., 2021; Fasola et al., 2022; and others) are well documented and operators use these methods routinely to optimize field development. It is much more challenging to track the provenance of produced fluids in more complex reservoirs like:

- naturally fractured reservoirs or structurally complex reservoirs (e.g., Rockies source rock plays),
- plays where the bulk of the oil is migrated from nearby kerogen-rich zones, e.g., Montney in the Alberta basin; Scoop and Stack plays, Anadarko basin; Niobrara Chalks in the DJ basin; and Turner in the Powder River basin.
- Pay zones where migrated high maturity gas has mixed or is interbedded with locally generated fluids, e.g., Montney in the Alberta basin; parts of the Wolfcamp in the Delaware basin.

Mobility of multi-phase fluids in the subsurface is strongly dependent on both geological history and operational activity. Reducing the uncertainty around the source of mobile oil, gas and water is essential for field management. Jones et al. (2021) show that in the Powder River basin produced oil and produced water provenance share some commonalities, but that water is produced from a larger rock volume than the oil. Compiling a large database of produced fluid and baseline reservoir fluids is essential for these more complex systems. The Montney study here showed that mud gas and produced liquids were important to decipher whole produced fluid provenance in a migrated play with additional high maturity gas. Especially in bubble point oil and wet gas reservoirs, reservoir flow units and the distribution of the kind of fluids in each pay zone must be understood before using geochemical data to fingerprint oil samples (Adams and Kornacki, 2019).

It is possible to assess the effective saturation pressure of each contributing fluid flow unit if the time lapse production allocation is carried out on the liquids *and* gas. The respective end-members are taken from cuttings and mud gas obtained from the same depths in the pilot hole, and from separator samples taken simultaneously (or as near-simultaneously as is practical) from each stream. As the DRV pressure depletes over time, each contributing fluid flow unit will eventually cross its saturation pressure, determined by the unique composition of the particular fluid in that flow unit. Those units which drop below the saturation pressure will preferentially produce the gas-phase, thereby increasing the aggregate GOR for the well and suppressing the flow contribution from the other units which are still flowing single phase. The in-situ saturation pressure for each flow unit can be deduced by observing relative contributions of oil and gas from each contributing flow unit at the time of each GOR increase, or rate of GOR increase. Bo from each fluid can be estimated from the respective oil and gas compositions at P_{RES} and T_{RES} (Petrosky and Farshad, 1998). Together, these inputs can deliver from each flow unit in the DRV the component production rates, decline curves (Flannery and Bennett, 2019), EURs, and recovery percentages. Production forecasts, reservoir models, well spacing, and other field development models can subsequently be tuned to each horizon with a sensitivity that is not possible without the resolution provided by geochemical time lapse allocation.

Recovery factor for each zone active in the DRV can be estimated by using the rock properties and the EZ-LTHP estimates of mobile oil, in combination with fluid properties and fluid saturations determined by NMR or other methods to get mobile OOIP for each zone or DRV of a given well. Paired with oil and gas production data and % contribution from each landing zone from a time-lapse production allocation analysis yields the zonal decline curves and zonal EUR (**Figure 7**). These data can be manipulated to calculate % recovery from each zone. Discontinuities in these decline curves or zonal contributions might point to an operational problem or that one or more of the contributing zones has reached its effective bubble point causing preferential gas production. This replicated over a whole field ought to show how each zone responds to different completions and well spacing. Lateral variations in oil quality, GOR or CGR and sorbed oil as a function of kerogen type and thermal maturity may also become apparent.

Mobile oil estimates and the geochemical fingerprinting can be leverage for EOR program design. The difference between the post-solvent extraction total oil and the EZ-LTHP mobile oil is a conservative estimate of recoverable oil via chemical or miscible flood EOR. If primary production leaves some mobile oil in the reservoir, then recovery potential via restimulation and classic EOR will be higher. If recovery factor has been calculated, a more accurate estimate of EOR recoverable oil using the chosen method will be possible. Of course, the EOR operation will most likely not be 100% efficient either, leaving some “unrecovered”, but theoretically, producible oil in the reservoir.

Miscible gas huff-and-puff EOR is suitable for tight unconventional plays (Gautam et al. 2023). These operations are traditionally monitored using the liquid production rate and the mass balance of flowback fluids compared to produced oil to determine the amount of injected gas that is produced back. However, following a geochemical allocation program, monitoring the changes in produced oil chemistry related to the miscible gas flood and the amount of injected gas recovered during flowback periods using gas isotopes can be used to further refine EOR operations.

The stable isotopes ($\delta^{13}\text{C}$ - $\text{C}_{\text{gas species}}$ and $\delta^2\text{H}$ - $\text{C}_{\text{gas species}}$) are conservative properties, which do not change significantly upon depressurization, solution or dissolution (van Graas et al., 2000). Therefore, stable isotope concentrations in natural gases are independent of reservoir and sampling conditions rendering themselves as useful tracers for many gas field operations. This type of monitoring does require the injection gas to have a different isotopic signature from the natural gas indigenous to the reservoir.

With regards to the oils, tight unconventional source rock plays show preferential paraffin production and abandonment of aromatic and heavier molecular weight compounds in the reservoir (Kornacki, 2021). As shown here, the immobile oil (or EOR recoverable oil) most likely sorbed onto kerogen might have a different geochemical fingerprint than the mobile oil, which will not be detected by solely monitoring the liquid production rate of an EOR operations. To identify the geochemical fingerprint of the EOR recoverable oil, we recommend analyzing the solvent extract from the post-LTHP rock material and comparing the types of compounds found in primary produced oil to EOR produced oil to identify additional compounds found in the core extracts are liberated by EOR operation. The different compounds from this sorbed oil can be tracked using production allocation technology on the flowback oil in a huff and puff operation. Production allocation of flowback oil and gas would also enable operators to accurately time the collection of new PVT samples for calibration of simulation work to maximize recovery and minimize operational costs of an EOR pilot.

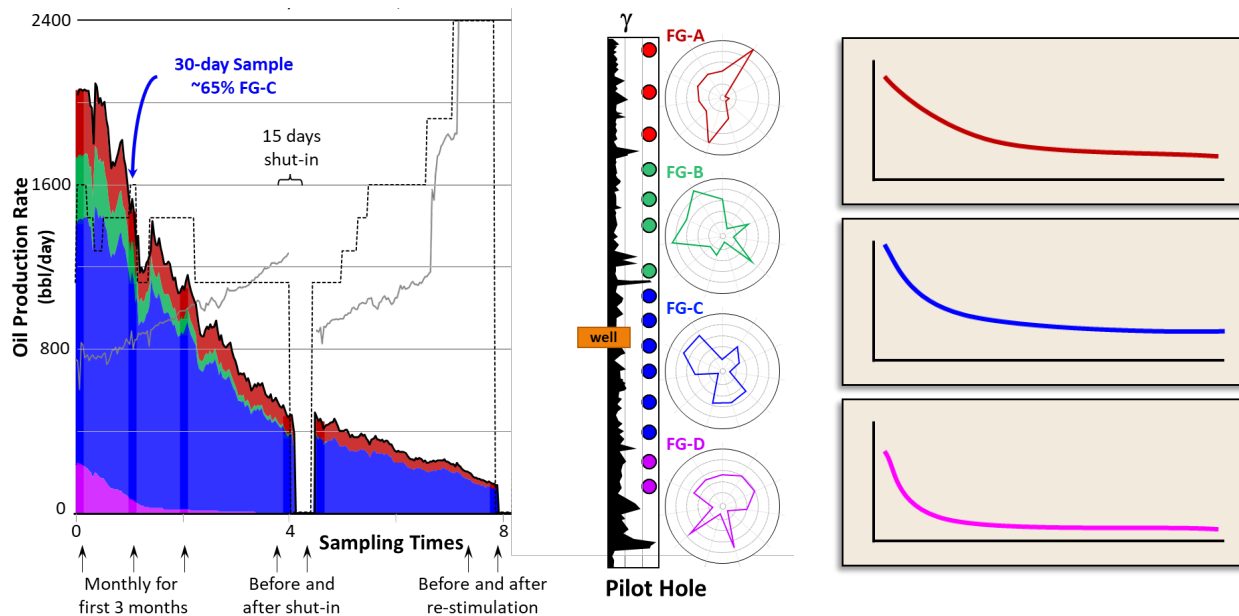


Figure 7. Example decline curves by contributing zone calculated from time lapse production allocation determinations (from Flannery and Bennett, 2019). GOR is shown in fine gray line and choke is shown as dashed line. Radar plots representative of the 4 end-member oil fingerprints from core extracts are shown for the 4 geochemical flow units (FG-A through FG-D).

Conclusions

Natural geochemical tracers can be effectively used to quantify zonal contributions to produced fluids, identify optimal PVT sampling times, better calibrate of reservoir models and establish zonal decline curves. Here we demonstrate that geochemical fingerprinting studies based on reservoir rock material from unconventional reservoirs are most successful, when tailored to the reservoir architecture of each play, drilling mud type (OBM vs. WBM), petroleum thermal maturity (subsurface liquid- through vapor-phase fluids) and end-member sample type (core, cuttings, pseudo end-member oils).

Our case studies from the Vaca Muerta play (Argentina) required center-cut core plugs due to use of OBM and showed that the organic-rich Cocina and Organico intervals in the Vaca Muerta expelled liquid into intervening good reservoirs. However, liquids dominantly are produced from the most organic-rich zones, with evidence of a larger drained rock volume (DRV) during early production. The large database of basic

geochemical source and maturity parameters measured on produced oils corroborate these findings can be used for on-going production monitoring to identify the impact of infill wells or out-of-zone production in new appraisal areas.

In the more structurally (Niobrara study) or geochemically more complex (Montney) plays, the assumption of uniform fluid mobility and stratigraphically bound flow units is overly simplistic. Zonal contributions are by matrix and fracture permeabilities, fluid pressures, pore size distributions and saturations, and fluid viscosities. Interbedded zones of indigenous Montney oil mixed with migrated more mature fluid – and major discontinuities in mud gas isotopes – document minimal vertical mixing. Horizontal wells produce gas and oil dominantly from better-quality reservoirs regardless of landing zone, with natural gas bypassing low permeability zones, resulting in different DRV's for produced gas and oil. Geochemically mapping *geological alteration/mixing* within a DRV and monitoring *operationally-induced fluid commingling* are powerful tools to optimize landing zones, well spacing, and well completions in the Montney play.

In the Niobrara example, total OOIP values based on pyrolysis are much higher in organic-rich (>1% TOC) target intervals than migrated reservoirs of the Codell Formation and match petrophysical log estimates but do not consistently represent Mobile Oil OOIP. We conclude that the high mobile/total oil zones contain only mobile, migrated oil only suitable for primary production and restimulation. Localized intervals of the Niobrara target zones have lower mobile/total oil than low TOC (<1%) non-source zones, meaning the Niobrara has good primary production and EOR potential. However, the pyrolysis data and production allocation results show that the best primary production and/or EOR zones are not necessarily co-incident with the highest TOC intervals, lithostratigraphy or even permeability.

The DJ Basin Study shows considerable contribution from the B Chalk and B Marl to produced oil regardless of landing zone due to structural complexity and the extensive natural fracture system. The substantial commingling in produced fluids is attributed to (i) well trajectories crossing multiple stratigraphic zones due to faulting; and (ii) hydraulic fractures tie into and enhance the natural fracture system. The observed mixing occurs on geological time frames (from natural fractures and faults) and operational time frames (from completions). Predicting well performance in such a system is very challenging, dictating very robust data integration.

For greater accuracy in predicting UR well performance, we present a method based on measured fluid and rock properties to target high mobile oil zones for primary production and identify prospective EOR recoverable oil zones. In unconventional tight source rock reservoirs, total oil values based on pyrolysis measurements match petrophysical log estimates, but greatly overestimate mobile OOIP. Use of the new EZ-LTHP method on wet WBM cuttings yields mobile oil volumes that are within 5-10% NMR mobile oil estimates. Total OOIP and Mobile oil estimates can be used to target most prospective zones for Primary production and EOR. The measured ratio of Mobile/Total oil can be used to correct total oil petrophysical logs, which are commonly adjusted based on general correlations to lithology and NMR wireline logs. Percent recovery by zone and zonal EURs (by optimizing choke management, well spacing, completion design, etc.) are achievable using a combination of physical measurements (poro-perm, NMR, pyrolysis) and time-lapse geochemical allocation, integrated with fluid and reservoir properties with production data.

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