

*Structural and hydrogeologic evolution of the Putumayo basin and adjacent fold-thrust belt, Colombia*

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**APPENDIX 1: FACTORS AFFECTING OIL QUALITY**

A combination of structural and hydrogeologic factors affects oil quality. These factors include the deformation history and trapping mechanisms, and the manner in which flow of meteoric water into reservoirs degrades light oil to heavy oil and tar.

Oil quality and mapping of degradation trends are important components of exploration risk assessment and block ranking consideration (Wenger et al., 2002; Yu et al., 2002). Degraded oils are extensive in foreland basins (Head et al., 2003). From deeply buried kitchens near the mountain front, oil may migrate updip  $\leq 200$  km into the distal foreland, in which degradation processes commonly contribute to the formation of heavy-oil deposits, such as the Athabasca Tar Sands of Canada (Tozer et al., 2014) and Orinoco heavy oil belt of Venezuela (Head et al., 2003). Structural or stratigraphic traps developed along the migration pathways may accumulate lighter oil. Thus, foreland basins such as the Putumayo basin may be expected to show a wide range of oil API gravity.

The API gravity of oil is a general indicator of oil quality (Macgregor, 1996). Several processes degrade light oil to heavier API gravity (Wenger et al., 2002; Head et al., 2003; Larter et al., 2003, 2006) and are summarized in Table 1 of the article. These processes include (1) compositional changes caused by water washing, biodegradation, cracking; (2) vertical leakage via fault leakage, erosion, or seal failure by overpressuring; and (3) lateral spillage caused by trap tilting, hydrodynamic flushing, or gas flushing.

**Compositional Changes: Water Washing, Biodegradation, and Cracking**

Water washing and biodegradation often occur in relatively shallow reservoirs (i.e.,  $<1830$  m) that are actively flushed by meteoric water (Palmer, 1993). The two processes always occur in tandem (Lafargue and Barker, 1988); however, at temperatures greater than  $80^{\circ}\text{C}$ , microbes causing oil biodegradation become inactive and water washing dominates (Lafargue and Barker, 1988). Water washing degrades oil by selectively removing lighter, water-soluble compounds such as benzene and toluene and decreasing API gravity, but otherwise causes minor changes in broader physical and chemical properties (Palmer, 1993). Oil fields with tilted oil-water contacts indicative of active groundwater flow (Hubbert, 1953) can be used to map areas where water washing may be occurring (Connan, 1984); however, after entrapment, water washing only occurs at the oil-water contact.

Biodegradation selectively consumes  $\text{C}_{10}\text{--}\text{C}_{24}$ , long-chain, normal alkanes most rapidly, particularly in reservoirs with low thermal gradients and shallow traps (Head et al., 2003). Biodegradation occurs at less than  $80^{\circ}\text{C}$ ; however, modern, cooler reservoirs that were charged at temperatures  $>80^{\circ}\text{C}$  may have been “paleopasteurized” so that microbes are not active (Wilhelms et al., 2001).

Effects of water washing and biodegradation can be similar and hard to distinguish (Wenger et al., 2002). Compared with unaltered oil, biodegradation

\*Deceased (November 6, 2014).

decreases API gravity and the amount of saturated hydrocarbons, and is more likely to produce tar (Lafargue and Barker, 1988). Biodegradation also increases density, acidity, viscosity, resins, asphaltenes, metals (e.g., Ni and V), and organic compounds containing N, S, and O (Blanc and Connan, 1993; Peters et al., 2005).

Laboratory experiments suggest that water washing occurs rapidly at annual timescales (Lafargue and Barker, 1988). Because biodegradation is diffusion controlled, rates are much slower than water-washing processes; therefore, millions of years may be required to degrade an entire reservoir (Head et al., 2003; Larter et al., 2003).

Compositional changes caused by cracking are not considered here because this study focuses only on potential processes that may degrade oil during migration and after entrapment.

### **Oil Leakage: Faulting, Erosion, Seal Failure, Trap Tilting, and Flushing**

High rates of oil degradation occur in compressional settings where traps are susceptible to fault leakage and seal bypass (Macgregor, 1996; Cartwright et al., 2007). In such settings, thrust faults, steep reverse faults, and asymmetric to overturned anticlines provide potential avenues for vertical leakage. Seals are also vulnerable to failure during exhumation, erosion, fracture development, tilting, and/or faulting. Tilting or further deformation of an original structural trap can cause oil to exit the trap at its spill point, with possible remigration to shallower structures (Macgregor, 1996; Parnell, 2002). Hydrodynamic flushing (discussed above for the associated process of water washing) may also occur in areas of high groundwater flux (Hubbert, 1953) such as the Athabasca Oil Sands of Canada (Garven, 1995).

The drill stem tests in the Putumayo basin (Figure 6F) exhibit normal to subnormal pressures throughout the basin, and prior seal failure by overpressure is not reported for producing fields or drilled prospects; thus, this study does not consider this process. Similarly, displacement of oil by gas flushing (Macgregor, 1996) has not been identified as an important process in the Putumayo basin.

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## APPENDIX 2: WELL DATABASE EXPLANATION

The well database is contained in this Microsoft Excel spreadsheet ([click here to download](#)). The first tab in the spreadsheet includes an explanation of the database. The second tab contains the well database.

The third tab includes well test results from drill stem tests, formation testing, and other public sources compiled as part of this study.

## APPENDIX 3: CALCULATION OF EQUIVALENT FRESHWATER HEAD

Equivalent freshwater head ( $H_0$ ) was calculated from formation pressure measured during well testing using

$$H_0 = \frac{P}{\rho_B g} + z \quad (1)$$

where  $P$  is in MPa,  $g$  is acceleration of gravity in  $\text{m sec}^{-1}$ ,  $\rho_B$  is equivalent freshwater density in  $\text{g cm}^{-3}$  corrected for pressure, temperature, and salinity at reservoir conditions, and  $z$  is elevation in m. Formation water salinity was taken from 93 chemical analyses available in information from the ANH and 360 measurements reported by A. Bejarano W. et al. (1990, 1991, personal communication), which were estimated from geophysical logs using standard approaches (Schlumberger, 1988).

Equivalent freshwater density  $\rho_w$ , which accounts for temperature and pressure in the reservoir, was calculated using the approach of Batzle and Wang (1992), which was used by Villegas et al. (1994) and Bachu (1995) in the Llanos basin

$$\rho_w = 1 + 1 \times 10^{-6} \left( \begin{array}{l} -80T - 3.3T^2 + 0.00175T^3 + 489P - 2TP + 0.016T^2P \\ -1.3 \times 10^{-5}T^3P - 0.333P^2 - 0.002TP^2 \end{array} \right) \quad (2)$$

where  $\rho_w$  is water density at formation pressure and temperature ( $T$ ) is °C. Bottomhole temperature was converted to formation temperature using approaches available in the open literature (Chapman et al., 1984; Bachu and Burwash, 1991). A correction for salinity effects was applied as

$$\rho_B = \rho_w + S \left\{ 0.668 + 0.44S + 1 \times 10^{-6} \left[ 300P - 2400PS + T \left( \begin{array}{l} 80 + 3T - 3300S \\ -13P + 47PS \end{array} \right) \right] \right\} \quad (3)$$

where  $S$  is mass fraction of NaCl in ppt/ $10^6$ .

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## APPENDIX 4: LIMITATIONS OF DATABASE AND STUDY APPROACH

Many wells in the database are over 10 yr old, and newer, possibly more successful, confidential wells were unavailable to this study. Thus, the mapping of well status (Figure 5) and evaluation of oil quality, formation water salinity, and reservoir attributes (Figures 6–8) may be biased to older, noneconomic wells in the public domain. Complete well geochemical analyses of oil and gas were not available. Also, the mapping of formation water  $\text{Cl}^-$  (Figure 7) used 75 salinity measurements measured during well testing. These were augmented with greater than 500 salinity values derived from petrophysical estimates of NaCl (A. Bejarano W. et al., 1991, personal communication), which may be less accurate than directly measured water  $\text{Cl}^-$ . In addition, the mapping of equivalent freshwater head (Figure 8) used 85 pressure measurements. These were acquired during well testing under field conditions under variable quality-control protocols and may not represent actual formation pressure conditions. Therefore, we cleaned the pressure data set by omitting implausible values that deviated from expected conditions or that resulted from obviously failed tests. In addition, both the formation water chloride concentration and pressure values were obtained at discrete depth intervals. Where multiple values existed for one well, these were grouped into three categories according to stratigraphic age by calculating the mean of the individual values. Finally, populating the domain of the groundwater model (i.e., along line of section AA' southeast of Palmera-1, shown in Figure 2) was complicated in that wells in this area are widely distributed—and well tests were conducted in the Cenozoic. Thus, the permeability field of the model based on the best available data and general trends was reported in the open literature.

Conversely, studies of hydrodynamic processes in the Llanos basin used a more extensive well

database. For example, detailed analyses from more than 300 wells, more than 40 of which with complete chemical analyses of formation water, were available to Person et al. (2012) and Villegas et al. (1994). Also in the Llanos basin, Gonzalez-Penagos et al. (2014) used an extensive database of geochemical and isotopic analyses for dozens of formation and surface water samples to infer salinity sources. Despite the differences in hydrogeologic data availability between the Putumayo basin and the Llanos basin, the approach used by this study still provides powerful insights into regional trends in oil and formation water quality in the Putumayo basin.

One of the primary limitations of the structural component of the study is the quality of seismic data. As also experienced by Villamil et al. (2004) in the Llanos basin, high-dipping reflectors generate weak returns. Thus, the critical fold-thrust belt is poorly imaged. As a result, structural interpretations must rely upon structural models.

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