Appendix L

Risk Assessment

APPENDIX L
Environmental Fate and Effects of Natural Gas Liquid Releases

When natural gas is removed from the ground, it is compositionally different than what is transported through natural gas transmission systems and ultimately used as an energy source for end users for home heating and cooking, and industrial energy. When removed from the ground, the mixture is predominately methane, but also includes heavier hydrocarbons and inert gases. Although the mixture can vary greatly, a typical natural gas stream may include 85 percent methane, 10 percent heavier hydrocarbons called natural gas liquids (NGLs), and 5 percent inert gases. NGLs usually are removed from natural gas during processing. Lighter ends, including propane and butane may be removed, stored and shipped separately. Alternatively, the operator may simply ship raw NGLs to a NGL plant for separation.

NGLs exist in fields as constituents of natural gas but are recovered separately as liquids. NGL should not be confused with natural gas, which is composed primarily of methane. NGL molecules liquefy more readily than methane. Overland Pass NGLs are composed of 53 percent ethane, 25 percent propane, 14 percent butane (normal and iso-), with smaller amounts (4 percent) of (iso) pentane, and pentane plus hexane and heptane (sometimes referred to as natural gasoline or plant condensate) (**Table L-1**). NGL is denser than natural gas and becomes combustible at different concentrations than methane.

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Table L-1 Composition of Overland Pass Pipeline NGLs

Component	Liquid Volume Percent
Methane	0.36
Ethane	53.16
Propane	25.75
Butanes	13.50
Pentanes	4.42
Hexanes +	2.61
BTEX	0.12
Carbon dioxide	0.11

Note: Specific gravity is 0.446

NGLs have a variety of different uses, including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy. They can also be used in many applications, such as:

- Ethane is primarily used for the production of plastics.
- Propane is typically used for heating purposes, gas grills, lanterns etc, but can also be used in the production of plastics.
- Butanes and natural gasoline are primarily used for motor gasoline blending

Properties and Hazards

Ethane (C_2H_6) exists as a colorless, odorless gas at ambient pressure and temperature. It is heavier than air and may concentrate in low-lying areas. Although ethane is not considered highly toxic it can replace oxygen molecules and cause asphyxiation.

Propane (C_3H_8) also exists as a gas at ambient pressure and temperature, but is heavier than air with 1.52 specific gravity as a vapor at 1 atmosphere and 60º F. (air = 1.0). Liquid Propane is lighter than water. It is about one-half as heavy as an equal volume of water.

Butane (C_4H_{10}) exists in both gaseous and liquid forms at ambient pressure and temperature, being less stable than propane in a gaseous form. Butane is heavier than air and heavier than propane. Its main use these days is industrial as a chemical feedstock (mostly after conversion to iso-butane), and is otherwise more waste than product.

Heavier NGLs (C5H12+), such as pentanes, hexanes, heptanes exist as liquids at ambient pressure and temperature and are shipped in liquid form. Heavier NGLs often are used as a diluent for shipping crude oil via pipeline; it reduces the viscosity of heavier crude oils.

Once released into the environment, NGLs are volatilized and quickly evaporate. NGLs are not generally toxic; however, as the gas takes the place of air, it becomes a simple asphyxiant and can cause suffocation from lack of oxygen. Hydrocarbon liquids shipped via pipelines generally have vapors that are heavier than air and that will collect in low or enclosed areas. These vapors are simple asphyxiants in that they will displace oxygen and create an oxygen-deficient atmosphere in those areas. NGLs are relatively non-toxic below the lower explosive limits (e.g., 30,000 ppm for ethane). Direct exposure to NGLs can result in frostbite to the skin and headache or nausea if inhaled. In addition, an accidental release of NGL, while in transport, may result in the following hazards:

- **POOL FIRES** - Upon release, heavier NGLs are flammable and, therefore, pose the hazard of thermal radiation.
- **FIREBALLS** - A large, pressurized release of a liquefied hydrocarbon such as propane or butane may burn in the form of a fireball, which grows larger and also moves upwards. Thermal radiation is the related hazard.
- **VAPOR CLOUD FIRES** - Upon release, propane or butane can form a vapor cloud that spreads horizontally. If little or no wind is present and atmospheric conditions are very stable, the spreading cloud mixes slowly with oxygen. It can burst into flames if ignited and flash back to the source of the release. Thermal radiation is the hazard.
- **VAPOR CLOUD EXPLOSIONS** - NGL vapor clouds are potentially explosive both in unconfined and confined situations. The hazard of such an explosion generally results from building damage or breaking windows.

Table L-2 provides a summary of the general chemical characteristics of NGLs.

Table L-2 Summary of Properties and Hazards

	Ethane	**n-Butane**	**Propane**	**Pentane+**
Formula	C2H6	C_4H_{10}	C3H8	C_5H12
Family	Hydrocarbon	Hydrocarbon	Hydrocarbon	Hydrocarbon
Appearance liquid	Colorless	Colorless	colorless	colorless
Appearance vapor	Foggy in concentration	Foggy in concentration	Foggy in concentration	Foggy in concentration
Odor	Odorless	Virtually odorless	Odorless	Odorless
Main hazard	Flammable	Flammable	Flammable	Flammable
BP@ATP	-88.6°C	-0.5°C	-42.1°C	°C
Flash point	-135°C	-60°0C	-105°C	°C
Flammable limits (LEL – UEL)	3.0-12.5%	1.9-9.0%	2.1-9.5%	%
Auto-ignition	515°C	405°C	450°C	°C
TLV[a]	No TLV	800 ppm critical effect narcosis	2500 ppm critical effect simple asphyxiant	600 ppm critical effects irritation and narcosis
Odor threshold	Odorless	5000 ppm	Odorless	Odorless
Reaction-air	No reaction	No reaction	No reaction	No reaction
Reaction - water	No dangerous reaction	No dangerous reaction	No dangerous reaction*	No dangerous reaction*

[a]ACGIH
*may form solid hydrates, insoluble.

Environmental Fate

Accidental releases of NGLs can occur during pipeline transport. Media distribution calculations according to Mackay Level 1 (1992) show that in the event of an accidental release of NGLs all of the material will end up in the air compartment due to the volatility of the hydrocarbons (API 2000).

Aerobic biodegradation of ethane is greater than 65% after 35 days (ZoBell 1963). API *Robust Summary of Information on Petroleum Gases* (2000) notes that ethane, propane and butane can be used by bacteria as carbon sources. When released into water, most of the NGLs will float to the surface where they will evaporate.

Evaporation will be the primary mechanism of loss for NGLs, rapidly reducing exposure and toxicity. Dissolution of NGLs in water is not a significant process (i.e., NGS are negligibly water soluble). Photodegradation of NGLs increases with greater solar intensity. It can be a significant controlling factor, especially of lighter products and constituents; but it will be less important during cloudy days and winter months.

Overall, the environmental fate of released NGLs is controlled by many confounding factors. Major factors affecting the environmental fate include spill volume, type of product, dispersal rate of the product, terrain, and weather. In the event of a leak, NGLs released from the pipeline would begin to vaporize, the gases would percolate through the soil and sediments, and then dissipate into the atmosphere. Only that component of the NGL stream that does not readily volatilize at atmospheric pressure (approximately 2 to 4 percent of the NGL) would remain to potentially migrate through the overlying surface materials and enter the groundwater. Once released, the physical environment largely dictates the environmental persistence of the spilled material. Generally, NGLs evaporate quickly and releases would be expected to rapidly dissipate.

Environmental Effects

If released into the environment, NGLs pose a range of risks to the environment and to human populations. NGLs shipped via pipelines generally have vapors that are heavier than air and that will collect in low or enclosed areas. These vapors are simple asphyxiants in that they will displace oxygen and create an oxygen-deficient atmosphere in those areas.

Hydrocarbon vapors are flammable or combustible, although different hydrocarbon liquids have different flash points (the temperatures at which sufficient flammable vapors are emitted) and flammable ranges (the range of vapor concentration in air expressed as a percentage by volume). This potential for flammability is likely the most serious threat to human health and the environment.

NGLs released to the environment may cause adverse biological effects on birds and mammals via inhalation exposure from highly volatile compounds. Acute toxic effects include narcotic effects, and possible death. While releases of NGLs may have an immediate and direct effect on wildlife populations, the potential for physical and toxicological effects attenuates quickly as the volume of material diminishes.

In mammals, high molecular weight alkanes are considered virtually nontoxic. Overall, NGLs have rapid rates of evaporation and low environmental persistence, thus the primary hazard from NGLs is considered to be acute, not chronic, airborne toxicity. Short-term impacts to vegetation in the area of a release may be possible. Aquatic toxicity of petroleum gases is not applicable.

Rats exposed to various concentrations of propane in air showed signs of central nervous system depression, intoxication and death. Recovery from a non-lethal exposure was rapid. The calculated effect concentration (EC_{50}) was 280,000 ppm (504,996 mg/m^3 (Clark & Tinson 1962). A similar study with isobutene resulted in an EC50 of 200,000 ppm (475,444 mg/m3). Hydrocarbons that volatilize into the atmosphere are broken down into smaller compounds by photodegradation and photo-oxidation

The behavioral responses of terrestrial wildlife may help reduce potential adverse effects. Many birds and mammals are mobile and will avoid leak areas. The greatest environmental impact of an NGL spill is the potential for fire and the resulting short-term ecological devastation.

Additional information regarding the fate of NGL and specific NGL components if accidentally released into the environment, including groundwater, can also be found in sections 4.3.4.1 and 4.3.4.2 of the Environmental Assessment for the Mid-America Pipeline Company, LLC (MAPL) Western Expansion Project. This Environmental Assessment was prepared by the BLM in 2005. The BLM's Environmental Assessment concluded that "a release from an NGL pipeline would result in the evaporation of most, if not all, of the liquids on the surface of the ground or in the vadose zone above the water table. Under certain conditions it would be possible for a very small portion of the release to reach the water table. Because of their slight solubility in water, contamination from NGLs would be limited to a few parts-per-million. These concentrations would be further reduced by diffusion and natural attenuation further reducing the risk to potential receptors." This Environmental Assessment is available at http://www.nm.blm.gov/nmso/mid_am_pipeline/mid_am_pipeline.htm.

Assessment of Worst Case Scenario

As noted, in the event of a pipeline rupture NGLS will mostly volatilize and quickly dissipate, thereby minimizing the potential impacts to both humans and ecological receptors. The product contains 0.12% benzene, which, if enough material is spilled, could impact aquatic organisms or humans ingesting drinking water from the contaminated source. The potential for impacts was investigated by evaluating a conservative scenario whereby a complete pipeline rupture is assumed to dump the entire spilled product directly into the water. Mixing is assumed to be immediate and complete and the aquatic organisms and humans are assumed to live in and drink water containing the estimated benzene concentration from that location. Acute and chronic exposure of organisms and ingestion of water by humans are examined.

The pipeline throughput is assumed to be 150,000 bpd. Two stream flows were evaluated; moderate (100 cfs) and high (1000 cfs). In addition, two occurrences were evaluated;

- Complete rupture of the pipeline, and
- 1% leak.

Benzene concentrations were estimated assuming:

- All of the spilled product from the leak or rupture goes into the water
- Benzene is completely solubilized in the water column

	Acute	Chronic	Drinking Water
Rupture Time:	1-hour	1-hour	1-hour
Averaging Time:	0-hours	168-hours (7-day)	24-hours
Toxicity Value:	7.4 mg/L	1.4 mg/L	0.005 mg/L

If 6,250 barrels of product are spilled to a moderate flow stream the potential benzene concentrations at that location will be at a level seven times the acute toxicity threshold. Concentrations would rapidly drop as the plume moves downstream. The occurrence interval for this scenario is greater than every 50,000 years. All other predicted water concentrations would be below the acute toxicity threshold in water (**Table L-3**). No long-term or chronic impacts would be expected (**Table L-4**); however, if the spill occurred directly into a drinking water source, the potential benzene concentration could exceed the corresponding MCL, if it is assumed that at least 62.5 barrels are spilled into the water (**Table L-5**). Based on the occurrence interval, the likelihood of an impact to drinking water is very low.

Table L-3 Comparison of the Acute Toxicity Threshold for Aquatic Life with Estimated Benzene Concentrations following Pipeline Rupture or Leak to Streams

Throughput – 150,000 bpd	Stream Flow Rate (cfs)	Benzene Acute Toxicity Threshold (mg/L)	Scenario[a] Complete rupture (6250 barrels) (mg/L)	1% Leak (62.5 barrels) (mg/L)	Projected Occurrence Interval[c] (# yrs between spills) Complete Rupture	1% Leak
Moderate Flow Stream	100	7.4	52[b]	0.5	51,496	23,303
High Flow Stream	1000	7.4	5	0.1	9,363	4,237

[a] Estimated proportion of benzene in the NGL is 0.12 percent, and is assumed to be entirely water solubilized in the event of a spill. The resulting concentration was calculated by multiplying 0.12 percent of the total amount of petroleum product released in 1 hour divided by projected stream flow volume. The model assumes uniform mixing conditions.

[b] Shading indicates concentrations greater than the acute toxicity threshold for aquatic species.
[c] Projected occurrence interval based on historical data from OPS hazardous liquids database.

Table L-4 Chronic Toxicity Threshold for Aquatic Life Compared with Estimated Benzene Concentrations following Pipeline Rupture or Leak to Streams

Throughput – 150,000 bpd	Stream Flow Rate (cfs)	Benzene Chronic Toxicity Threshold[a] (mg/L)	Scenario[b] Complete rupture (19,563 barrels) (mg/L)	1% Leak (221 barrels) (mg/L)	Projected Occurrence Interval[c] (# yrs between spills) Complete Rupture	1% Leak
Moderate Flow Stream	100	1.4	1.0	0.56	189,600	51,496
High Flow Stream	1000	1.4	0.1	0.06	34,473	9,363

[a] The chronic toxicity value for benzene is based on a 7-day chronic toxicity value of 1.4 mg/L for trout. Exposure concentrations were estimated over a 7-day period since the chronic toxicity value was based on a 7-day exposure.
[b] Estimated proportion of benzene in the petroleum product is 0.12 percent, and is assumed to be entirely water solubilized in the event of a spill. The resulting concentration was calculated by multiplying 0.12 percent of the maximum amount of petroleum product divided by 7 days of stream flow volume. The model assumes uniform mixing conditions.
[c] Projected occurrence interval based on historical data from OPS hazardous liquids database.

Table L-5 Human Drinking Water Standard Compared with Estimated Benzene Concentrations following Pipeline Rupture or Leak to Streams

Throughput – 150,000 bpd	Stream Flow Rate (cfs)	Benzene MCL (mg/L)	Scenario[a] Complete Rupture (6250 barrels) (mg/L)	1% Leak (62.5 barrels) (mg/L)	Projected Occurrence Interval[c] (# yrs between spills) Complete Rupture	1% Leak
Moderate Flow Stream	100	0.005	2.2[b]	0.02	51,496	23,303
High Flow Stream	1000	0.005	0.02	0.002	9,363	4,237

[a] Estimated proportion of benzene in the petroleum product is 0.12 percent, and is assumed to be entirely water solubilized in the event of a spill. The resulting concentration was calculated by multiplying 0.12 percent of the amount of petroleum product released in 1 hour during a pipeline rupture by 24 hours of stream flow.
[b] Shading indicates concentrations that could exceed the maximum containment level (MCL) for drinking water (0.005 mg/L).
[c] Projected occurrence interval based on historical data from OPS hazardous liquids database.

References:

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