Appendix F

Cliff Spring Action Level Memo

MEMORANDUM

To: Avila Tank Farm Collaborative Assessment Team

From: Charles Lambert, and Rebecca Countway, McDaniel Lambert;
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Date: April 4, 2008

Re: FINAL "Action Levels" for Cliff Springs Seeps

In November 2007, McDaniel Lambert, Inc. completed a screening Human Health Risk Assessment (sHHRA) to evaluate the possible human health impacts from potentially petroleum-impacted water seeping from the cliff springs at the former Avila Tank Farm (McDaniel Lambert, 2007). The sHHRA concluded that, based on maximum chemical concentrations detected in seep samples collected through May 2007, there are no significant risks to beach users, even when unrealistically high contact with water seeping from the cliff springs along Avila Beach adjacent to the former Avila Tank Farm is assumed as the exposure scenario.

ARCADIS BBL performed an ecological risk evaluation on the seep data, which was presented in the Addendum to the Predictive Ecological Risk Assessment of On Site Wetlands (pERA) (ARCADIS BBL, 2007). The evaluation of the cliff springs focused on the aquatic invertebrate and algae population that potentially inhabit the seeps. The pERA concluded that the potential for ecological risk due to exposure to the cliff springs water is minimal.

In order to ensure the protection of future beach goers and ecological receptors that may be exposed to the seeps, the California Central Coast Regional Water Quality Control Board (RWQCB) requested that the development of "action levels" for the cliff spring seeps – concentrations of chemicals that would trigger the re-evaluation of potential health risks from seeping water. This memorandum addresses this request, and the following action levels are recommended.

Potential risks to beach goers should be re-evaluated if:

- An orally/derrmally carcinogenic polycyclic aromatic hydrocarbon (PAH), specifically benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, or indeno(1,2,3-cd)pyrene, is detected in future seep samples. Reporting limits for the PAHs should be on the order of 0.00009 mg/L; or
- Total petroleum hydrocarbon (TPH) concentrations exceed 7 mg/L.

Potential risks to ecological receptors should be re-evaluated if:

- A carcinogenic PAH (specifically benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, or indeno(1,2,3-cd)pyrene) is detected in future seep samples. Reporting limits for the PAHs should be on the order of 0.00009 mg/L; or

- A non-carcinogenic PAH (specifically anthracene, fluorene, naphthalenes [including methylnaphthalenes] or phenanthrene) exceeds the lowest chronic water quality benchmarks for non-carcinogenic PAHs of 0.00073 mg/L; or
- TPH concentrations exceed 2.48 mg/L.

Background

The cliff springs are ephemeral, year-round, and emergent features that are present in years with average or above average rainfall (RWQCB Staff). These springs have highly variable seasonal flow volumes, however, when there is flow the volumes are so low as to make sample collection difficult (Mike Rendina, Avocet – personal communication). The water does not pool at the base of the cliffs, but rather is rapidly absorbed by the sand. To be exposed to this water, a person would have to have contact with the water as it flows down the surface of the cliff face.

Water from the seeps has been sampled since February 1998. As of May 2007, only two chemicals have been detected in the seep samples, TPH and the PAH naphthalene. Petroleum hydrocarbons have been detected in 50% of the 68 samples analyzed for this constituent, with concentrations ranging from 0.089 to 1.7 mg/L. Naphthalene has been detected only once in the 57 samples analyzed, at a concentration of 0.00030 mg/L (see Table 1 in McDaniel Lambert, 2007).

In order to be health protective, the human health screening evaluation (McDaniel Lambert, 2007) assumed that the seeping springs result in hypothetical wadeable pools of water, with dermal exposure to hands, forearms, lower legs, and feet and a water ingestion rate equivalent to that of a swimmer (0.05 L/day). The hypothetical cliff spring recreational user was assumed to come into contact with the springs for one hour per day, 58 days per year, for nine years (ages 7 through 16). The screening health assessment estimated the cancer risk to hypothetical waders to be $1.7x10^{-6}$, within the 10^{-4} to 10^{-7} risk management range stipulated by the USEPA (1990), and is below the Cal/EPA Proposition 65 point of departure (10^{-5}) (see Table 8, McDaniel Lambert, 2007). This cancer risk was driven largely (45%) by dermal contact with nondetect concentrations of benzo(a)pyrene (BaP) in cliff springs water. Only one PAH was detected (naphthalene), therefore BaP was included in the assessment and evaluated at half the minimum reporting limit. Naphthalene is not considered carcinogenic via the oral pathway. Given that no carcinogenic PAHs (via the oral pathway) were detected, the actual cancer risk is less than $1x10^{-6}$. Furthermore, the estimated noncancer hazard is below the level of concern of 1.0.

The pERA evaluated potential risk from direct contact of ecological receptors to cliff spring water. The Avila cliff spring flow is intermittent and on a nearly vertical surface and is therefore considered limited in habitat potential. Filamentous algae are the only organisms that have been observed on site which may be chronically exposed to cliff spring water, but invertebrate exposure may occur, and was assessed as well. Wildlife ingestion of cliff spring water was not considered a viable pathway. Potential ecological risk from cliff spring water was assessed by comparing detected concentrations to available water quality benchmarks which are protective of aquatic life.

Risk-Based Action Levels for the Protection of Human Health

One approach for identifying action levels for the cliff springs seeps is to calculate risk-based screening levels - chemical concentrations in water that are below thresholds of concern for human health risks. The calculation of safe screening levels utilizes the exposure and toxicity information used for the estimation of risks as in the sHHRA, but combines them in a manner to identify the concentration of each chemical that results in a target risk level that is considered to

be safe (e.g., cancer risk within the 10^{-4} to 10^{-7} risk management range stipulated by the USEPA (1990), or noncancer hazard of 1.0).

Specifically, action levels for the seeps can be calculated for non-cancer and cancer health can be determined using the exposure and toxicity information from the sHHRA based on the following equations. For carcinogenic effects:

*Seep screening level = Target LICR / ((IFo*CSFo) + (IFd*CSFo))*

where:

Seep Screening Level = Health-Protective Level (mg/L)
Target LICR = Lifetime Incremental Cancer Risk = 1×10^{-6}
IFo = oral intake factor
IFd = dermal intake factor
CSFo = oral cancer slope factor

For non-carcinogenic effects:

Seep screening level = Target Hazard Quotient / ((IFo/RfDo) + (IFd/RfDo))

where:

Seep Screening Level = Health-Protective Level (mg/L)
Target Hazard Quotient = 1.0
IFo = oral intake factor
IFd = dermal intake factor
RfDo = oral reference dose

Tables from the sHHRA presenting the toxicity factors, dermal permeability constants, and exposure parameters are included in Attachment 1. The results of these screening level calculations, for all chemicals of potential concern identified in the sHHRA, are presented in Table 1 below. Screening levels based on the carcinogenicity of PAHs are very low, ranging from 0.00006 mg/L for BaP to 0.008 mg/L for chrysene. Noncancer screening levels for PAHs are much higher, ranging from 1.9 mg/L for indeno(1,2,3-cd)pyrene to 130 mg/L for phenanthrene. The calculated noncancer screening level for petroleum hydrocarbons is 7.7 mg/L, which conservatively assumes that the TPH is comprised 100% of the more toxic aromatic fraction.

Table 1. Human Health Risk-Based Seep Screening Levels for Hypothetical Cliff Spring Recreator

CHEMICAL	Hypothetical Cliff Spring Recreational User		
	Cancer Screening Level	NonCancer Screening Level	Minimum Screening Level
PAHs			
Acenaphthene	NC	3.81E+01	3.81E+01
Acenaphthylene	NC	3.30E+01	3.30E+01
Anthracene	NC	1.17E+02	1.17E+02
Benz(a)anthracene	8.89E-04	4.11E+01	**8.89E-04**
Benzo(b)fluoranthene	6.02E-04	3.71E+00	**6.02E-04**
Benzo(k)fluoranthene	6.87E-04	4.24E+00	**6.87E-04**
Benzo(g,h,i)perylene	NC	2.29E+00	2.29E+00
Benzo(a)pyrene	6.02E-05	2.79E+00	**6.02E-05**
Chrysene	8.89E-03	4.11E+00	**8.89E-03**
Dibenz(a,h)anthracene	8.29E-05	1.31E+01	**8.29E-05**
Fluoranthene	NC	1.14E+01	1.14E+01
Fluorene	NC	2.22E+01	2.22E+01
Indeno(1,2,3-cd)pyrene	4.23E-04	1.96E+00	**4.23E-04**
1-Methylnaphthalene	NC	4.47E+00	4.47E+00
2-Methylnaphthalene	NC	4.47E+00	4.47E+00
Naphthalene	NC	2.23E+01	2.23E+01
Phenanthrene	NC	1.30E+02	1.30E+02
Pyrene	NC	6.23E+00	6.23E+00
Total Petroleum Hydrocarbons*			
TPH	NC	7.77E+00	7.77E+00

Concentrations are in mg/L.
NC = No criteria.
Bold text indicates minimum screening level is based on potential cancer risks.
*TPH screening levels conservatively assume that the TPH is 100% biased to the more toxic aromatic fraction.

As demonstrated by the much lower screening levels, cancer is the endpoint of concern for PAHs. In fact, the noncancer screening level concentrations are generally higher than the water solubility of PAHs, which range from 0.0005 mg/L for dibez(a,h)anthracene to 3.9 mg/L for acenaphthylene (ATSDR, 1995). It is important to keep in mind that, to date, none of these orally/dermally carcinogenic PAHs have been detected in the seep water samples. The reporting limits for these PAHs, analyzed via EPA Method 8270 SIM, have ranged from 0.000094 to 0.0020 mg/L, with the most recent analyses by Test America all between 0.000094 to 0.000097 mg/L (Avocet, 2007). These reporting limits are very close to the calculated screening values for the hypothetical seep receptor. Given the very conservative exposure parameters used to describe the hypothetical seep recreator, the slight difference between the lowest screening levels and the recent reporting limits are very unlikely to result in any real health risks.

Risk-Based Action Levels for the Protection of Potential Ecological Receptors

The approach proposed for the protection of human health also was evaluated from an ecological perspective. The current detection limits for carcinogenic PAHs are less than acute or chronic

water quality benchmarks.[1] Therefore, the use of a detected concentration as a criterion for evaluating exposure further is adequately conservative. However, the approach for human health does not specifically address noncarcinogenic PAHs (e.g., anthracene, acenaphthene, acenaphthylene, benzo(g,h,i)perylene, fluoranthene, fluorene, naphthalene, 1- and 2-methylnaphthalene, phenanthrene, and pyrene).[2] Because the noncarcinogenic PAHs generally have lower molecular weight than the carcinogenic PAHs, they are more water soluble and more likely to result in exposure to ecological receptors than the heavier, less soluble carcinogenic PAHs. Therefore, to adequately address the potential for ecological risks in the future, available chronic water quality screening levels for noncarcinogenic PAHs were identified (Table 2).

Table 2. Ecological Water Quality Benchmarks for Noncarcinogenic PAHs

Polycyclic Aromatic Hydrocarbon	Chromic Screening Level	Source
Acenaphthene	0.023	Suter & Tsao, 1996
Acenaphthylene	NV	
Anthracene	0.00073	Suter & Tsao, 1996
Benzo(g,h,i)perylene	NV	
Fluoranthene	0.006	Suter & Tsao, 1996
Fluorene	0.0039	Suter & Tsao, 1996
1-Methylnaphthalene	0.0021	Suter & Tsao, 1996
2-Methylnaphthalene	NV	
Naphthalene	0.012	Suter & Tsao, 1996
Phenanthrene	0.0063	Suter & Tsao, 1996
Pyrene	NV	

Concentrations are in mg/L.
NV = No Value

None of the available PAH benchmarks listed above are below the SIM detection limits (as described above at 0.000094 to 0.000097 mg/L), therefore it is proposed that the action level for non-carcinogenic PAHs be the lowest available PAH water quality benchmark protective of ecological receptors. This would result in a non-carcinogenic PAH threshold of 0.00073 mg/L.

For TPH, there are no aquatic life benchmarks. Therefore, it is proposed that the TPH benchmark used in the pERA of 2.48 mg/L be used as the TPH threshold for the cliff springs. This value is based on the risk management goal for aquatic invertebrates developed for the Former Guadalupe Oil Field.

Recommended Action Levels

For the continued protection of beachgoers and the environment, human health and ecological action levels for the cliff spring seeps – concentrations of chemicals that would trigger the re-evaluation of potential health risks from seeping water – were determined.

It is recommended that the potential risks from the seeps to beachgoers be re-evaluated if there is a detection of any of the carcinogenic PAHs in water collected from the seeps, assuming

[1]Although carcinogenicity is not an endpoint for aquatic receptors, the language has been retained based on the results of the human health evaluation and the terms carcinogenic and non-carcinogenic as used as general references to the low and high molecular weight PAHs.
[2]Naphthalene is not considered a human carcinogen via the ingestion/dermal pathways.

analytical detection limits on the order of 0.00009 mg/L, or if detected concentrations of TPH exceed 7 mg/L. The screening level of 7 mg/L for TPH is conservative, as it assumes that the TPH is comprised wholly of the aromatic fraction.

For the continued protection of ecological receptors, it is recommended that potential ecological risks be re-evaluated if there is a detection of a carcinogenic PAH, if there is a detection of a non-carcinogenic PAH greater that 0.00073 mg/L, or if TPH is detected at a concentration of TPH greater than 2.48 mg/L.

References

Agency for Toxic Substance and Disease Registry (ATSDR). 1995. Toxicological Profiles for Polycyclic Aromatic Hydrocarbons. August.

ARCADIS BBL. 2007. Addendum to the Predictive Ecological Risk Assessment An Assessment of On Site Wetlands, UNOCAL Avila Tank Farm, San Luis Obispo County, California. Prepared for the Avila Tank Farm Collaborative Assessment Team. Ratified November 2007.

Avocet Environmental, Inc. 2007. Excel workbook summarizing Avila Tank Farm Cliff Springs data. July 8.

McDaniel Lambert, Inc. 2007. Memorandum: FINAL Screening Human Health Risk Assessment for the Cliff Springs at the Former Avila Tank Farm. November 20, 2007. Ratified by the Avila Tank Farm Collaborative Assessment Team, December 2007.

Suter, G.W. and C.L. Tsao. 1996. Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota: 1996 Revision. Oak Ridge National Laboratory, Oak Ridge, TN. June. ES/ER/TM-96/R2.

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). 1997. Volume 3. Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Amherst Scientific Publishers. July.

U.S. Environmental Protection Agency (USEPA). 1990. National Oil and Hazardous Substances Pollution Contingency Plan, Final Rule. Federal Register, Vol. 55, No. 46, Rules and Regulations, March 8.

ATTACHMENTS

ATTACHMENT 1
sHHRA Toxicity Factors, Dermal Permeability Constants, and Exposure Parameters

Table 2
Chemicals of Potential Concern Toxicity Criteria

CHEMICAL	Cancer Slope Factors (CSF)		Noncancer Reference Doses (RfD)	
	Oral CSF (mg/kg-day)$^{-1}$	Source	Oral RfD (mg/kg-day)	Source
PAHs				
Acenaphthene	NC		6.00E-02	IRIS
Acenaphthylene	NC		6.00E-02	*Ace (IRIS)*
Anthracene	NC		3.00E-01	IRIS
Benz(a)anthracene	1.20E+00	Cal/EPA	3.00E-01	*Anth (IRIS)*
Benzo(b)fluoranthene	1.20E+00	Cal/EPA	4.00E-02	*Fluoranth (IRIS)*
Benzo(k)fluoranthene	1.20E+00	Cal/EPA	4.00E-02	*Fluoranth (IRIS)*
Benzo(g,h,i)perylene	NC		3.00E-02	*Pyrene (IRIS)*
Benzo(a)pyrene	1.20E+01	Cal/EPA	3.00E-02	*Pyrene (IRIS)*
Chrysene	1.20E-01	Cal/EPA	3.00E-02	*Pyrene (IRIS)*
Dibenz(a,h)anthracene	4.10E+00	Cal/EPA	3.00E-01	*Anth (IRIS)*
Fluoranthene	NC		4.00E-02	IRIS
Fluorene	NC		4.00E-02	IRIS
Indeno(1,2,3-cd)pyrene	1.20E+00	Cal/EPA	3.00E-02	*Pyrene (IRIS)*
1-Methylnaphthalene	NC		4.00E-03	*2-MethNa (IRIS)*
2-Methylnaphthalene	NC		4.00E-03	*IRIS*
Naphthalene	NC		2.00E-02	*OEHHA (IRIS)*
Phenanthrene	NC		3.00E-01	*Anth (IRIS)*
Pyrene	NC		3.00E-02	IRIS
Total Petroleum Hydrocarbons				
Aliphatic TPH	NC		1.00E-01	TPHCWG
Aromatic TPH	NC		3.00E-02	TPHCWG

NC = No Criteria

Sources:
Cal/EPA = California Office of Environmental Health Hazard Assessment (OHHEA) Toxicity Criteria Database (Cal/EPA 2007)
OEHHA = Human-Exposure-Based Screening Numbers Developed to Aid Estimation of Cleanup Costs for Contaminated Soil (Cal/EPA 2005)
IRIS = USEPA's Integrated Risk Information System (http://www.epa.gov/iris/) (USEPA 2007)
TPHCWG = Total Petroleum Hydrocarbon Work Group
Italics indicate criteria for surrogate compound applied: "Ace" = acenaphthene, "Fluoranth" = fluoranthene, and "Anth" - anthracene.

Table 5
Chemical Specific Expsoure Parameters

CHEMICAL	Dermal Permeability Consant	Source
PAHs		
Acenaphthene	0.092	calculated
Acenaphthylene	0.11	calculated
Anthracene	0.16	calculated
Benz(a)anthracene	0.47	USEPA RAGS Part E
Benzo(b)fluoranthene	0.70	USEPA RAGS Part E
Benzo(k)fluoranthene	0.61	calculated
Benzo(g,h,i)perylene	0.85	calculated
Benzo(a)pyrene	0.70	USEPA RAGS Part E
Chrysene	0.47	USEPA RAGS Part E
Dibenz(a,h)anthracene	1.5	USEPA RAGS Part E
Fluoranthene	0.22	USEPA RAGS Part E
Fluorene	0.11	calculated
Indeno(1,2,3-cd)pyrene	1	USEPA RAGS Part E
1-Methylnaphthalene	0.047	naphthalene
2-Methylnaphthalene	0.047	naphthalene
Naphthalene	0.047	USEPA RAGS Part E
Phenanthrene	0.14	USEPA RAGS Part E
Pyrene	0.31	calculated
Total Petroleum Hydrocarbons		
Aromatic TPH	0.24	Obtained by averaging Kp values for aliphatic C8-C35; see below

Sources:
USEPA RAGS Part E = 2004 Risk Assessment Guidance for Superfund (RAGS), Vol., I, Part E (Supplemental Guidance for Dermal Risk Assessment); ABS are from Exhibit 3-4

Carbon Group	MW	log Kow	Chemical/Surrogates	Log Kp	Kp (cm/hr)
aliph C_{5-6}	86.17	4.11		-0.569952	0.269183
aliph $>C_{6-8}$	114.23	5.15		-0.040688	0.910567
arom C_{5-7}	78.11	2.13	benzene as surrogate	-1.831616	0.014736
arom $>C_{7-8}$	106.20	3.13	ethylbenzene as surrogate	-1.32892	0.046890
aliph $>C_{8-10}$	142.29	6.25		0.528176	3.374240
aliph $>C_{10-12}$	170.33	7.24		1.024552	10.581616
aliph $>C_{12-16}$	226.40	8.25		1.37716	23.831973
arom$>C_{8-10}$	134.22	4.01	isobutylbenzene as surrogate	-0.905032	0.124442
arom$>C_{10-12}$	162.28	5.52	n-hexylbenzene as surrogate	-0.065568	0.859868
arom$>C_{12-16}$	168.24	4.63	4-methylbiphenyl as surrogate	-0.686344	0.205900
aliph$>C_{16-35}$	226.40	8.25	n-hexadecane as surrogate	1.37716	23.831973
arom$>C_{16-35}$	168.24	4.63	4-methylbiphenyl as surrogate	-0.686344	0.205900
NA	154.21	3.98	Acenaphthene	-1.0367816	0.091879
NA	152.20	4.07	Acenaphthylene	-0.9660931	0.108120
NA	178.23	4.54	Anthracene	-0.8017048	0.157868
NA	252.31	6.06	Benzo(k)fluoranthene	-0.2133629	0.611839
NA	278.30	6.5	Benzo(g,h,i)perylene	-0.06848	0.854122
NA	166.22	4.18	Fluorene	-0.9720432	0.106649
NA	202.26	5.18	Pyrene	-0.513828	0.306318

Note:
LogKp = -2.80 + 0.66 logKow - 0.0056*MW (USEPA 2004, Equation 3.8)
kp = permeability constant in centimeters per hour
Carbon Group Information regarding Kow from TPHCWG, vol 3, p 33 - 38
PAH Information regarding Kow from ATSDR

Table 6
Intake Factors for Exposure Via Ingestion of Seep Water

Oral Seep Water Intake Factor (IForal):

$$IF_{oral} = \frac{IngR \times EF \times ED}{BW \times AT}$$

IF_{oral} = Oral Intake Factor, L water/kg body weight-day
IR = Ingestion Rate, L/day
EF = Exposure Frequency, days/year
ED = Exposure Duration, years
BW = Body Weight, kg
AT = Averaging Time, days

Exposure Variable	Hypothetical Cliff Spring Recreational User
IngR	0.05
EF	58
ED	9
BW	43
$AT_{carcinogens}$	25550
$AT_{nonarcinogens}$	3285

PATHWAY-SPECIFIC INTAKE FACTORS:

Chemical-Specific Intake Factors via Water Ingestion (IF_{oral}), L water/kg body weight-day

Carcinogens x BF	2.38E-05
Noncarcinogens x BF	1.85E-04

Table 7
Intake Factors for Dermal Exposure to Seep Water

Dermal Water Intake Factor (IFdermal):

$$IF_{dermal} = \frac{SA \times PC \times CF \times ET \times EF \times ED}{BW \times AT}$$

IF_{dermal} = Dermal Intake Factor, L water/kg body weight-day
SA = Surface Area, cm^2
PC = Dermal Permeability Constant, cm/hour
CF = Volumetric Conversion Factor, 1 Liter/1000 cm^3
ET = Exposure Time, hours/day
EF = Exposure Frequency, days/year
ED = Exposure Duration, years
BW = Body Weight, kg
AT = Averaging Time, days

Exposure Variable	Hypothetical Cliff Spring Recreational User
SA	4093
CF	0.001
ET	1
EF	58
ED	9
BW	43
$AT_{carcinogens}$	25550
$AT_{nonarcinogens}$	3285

PATHWAY-SPECIFIC INTAKE FACTORS:
Chemical-Specific Intake Factors via Dermal Water Contact (IF_{dermal}),L water/kg body weight-day

Carcinogens x PC	1.94E-03
Noncarcinogens x PC	1.51E-02