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File # 13-00142

March 7, 2014

Petroleum Technology Alliance of Canada
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Attention: Tannis Such

**RE: Comparison of Vapour Emissions from Remediation by *Ex-situ*
Excavation and Landfill Disposal – 2013 Sampling Program**

INTRODUCTION

Under the authorization of the Petroleum Technology Alliance of Canada (PTAC) Millennium EMS Solutions Ltd. (Millennium), has completed additional vapour sampling as part of an ongoing project assessing the environmental significance of vapour emissions during *ex-situ* remediation activities. The work was conducted under the Alberta Upstream Petroleum Research Fund (AUPRF), under the direction of the Canadian Association of Petroleum Producers (CAPP) and the Explorers and Producers Association of Canada (EPAC).

A spreadsheet model (the model) had been previously developed in 2010 to compare emissions from *ex-situ* remediation to landfill disposal. A preliminary attempt to calibrate the model and confirm modelling assumptions using actual emissions data from an ongoing remediation project was also completed in 2012. However, the data collected for the sampling were insufficient to confirm model validity.

SCOPE OF WORK AND OBJECTIVES

In order to complete validation of the original *ex-situ* emission model, MEMS and CAPP attempted to identify additional candidate sites undergoing *ex situ* remediation of volatile petroleum hydrocarbons (PHC). Candidate sites required concentrations of volatile hydrocarbons above guidelines and an appropriate remediation method being used. One potential candidate site was identified by CAPP but the attempts to contact those doing the remediation were unsuccessful. One candidate site initially identified by MEMS, but prior to remediation the approach was changed to excavation and landfilling. One other site identified by MEMS, a former gas plant site with volatile hydrocarbon contamination, was found to have volatile contamination above guidelines being remediated using an allu (TM) bucket and was retained for field validation of the model.

Sampling of soil and air for PHCs during planned *ex-situ* remediation activities was coordinated, with the purpose of comparing the measured air concentrations to the values predicted by the model, and using the soil concentrations to estimate the overall volume of contamination to be excavated and landfilled. The overall objective of the sampling program was additional validation of the model and determining if additional calibration of the model inputs was necessary.

DATA COLLECTION

Soil and air samples were collected simultaneously after a ten minute warm-up period for the operators and equipment. A total of ten soil samples and three air samples were collected. Soil samples were collected as grab samples from throughout the contaminated material in order to determine the overall average contamination of the soil prior to and after treatment by *ex-situ* remediation. Samples SS13-01 through SS13-05 were collected prior to treatment, and samples SS13-06 through SS13-10 were collected after treatment. Air samples were collected with flow-regulated summa canisters over a period of 1-hour from locations adjacent to the onsite emission sources (CLOSE), 10 m from the onsite emission sources (10M), and at a background location upwind of onsite vapour sources (CONTROL). Collection of soil and air samples occurred simultaneously, with the intention that the concentrations in the collected soil samples were representative of the resulting emissions from the *ex-situ* remediation processes.

Collected soil and air samples were submitted to ALS Laboratories in Calgary for analysis of benzene, toluene, ethylbenzene, xylenes, styrene, PHC F1, and PHC F2. Analysis of PHC F3, PHC F4, and moisture content was also completed for the soil samples. Testing of the physical characteristics of soil samples was completed on three composites generated from the existing ten soil samples.

RESULTS

In pre-treatment soil, ethylbenzene was detected in two samples (0.513 mg/kg and 0.071 mg/kg). PHC F1 (including BTEX) was detected in all samples, at concentrations ranging from 83 mg/kg to 897 mg/kg. PHC F2 was detected in three of the analyzed soil samples, at concentrations up to 44 mg/kg. PHC F3 and PHC F4 were not detected in any of the pre-treatment soil samples. Benzene, toluene, xylenes, and styrene were not detected in any pre-treatment samples. The average total PHC concentration in pre-treatment samples was 319 mg/kg.

In post-treatment soil samples, ethylbenzene was detected in one sample (0.074 mg/kg). PHC F1 (including BTEX) was detected in all samples, at concentrations ranging from 60 mg/kg to 594 mg/kg. PHC F2 was detected in one sample (25 mg/kg), and PHC F3 and PHC F4 were not detected. The average total PHC concentration in post-treatment samples was 190 mg/kg. Benzene, toluene, xylenes, and styrene were not detected in any post-treatment samples. The overall average decrease in soil PHC concentration from *ex-situ* treatment was 129 mg/kg.

Benzene (0.64 $\mu\text{g}/\text{m}^3$), toluene (1.24 $\mu\text{g}/\text{m}^3$), ethylbenzene (1.17 $\mu\text{g}/\text{m}^3$), xylenes (15.7 $\mu\text{g}/\text{m}^3$), PHC F1 (651 $\mu\text{g}/\text{m}^3$), and PHC F2 (210 $\mu\text{g}/\text{m}^3$) were detected in the CLOSE air sample. Only PHC F1 (574 $\mu\text{g}/\text{m}^3$) and PHC F2 (204 $\mu\text{g}/\text{m}^3$) were detected in the 10M sample, and only PHC F1 (28 $\mu\text{g}/\text{m}^3$) was detected in the CONTROL sample. The results of the laboratory analysis for soil and air samples are presented in Tables 1 and 2, respectively.

Table 1 Results of Soil Analyses													
Sample	SS13-1	SS13-2	SS13-3	SS13-04	SS13-5	SS13-6	SS13-7	SS13-8	SS13-9	SS13-10	COMP 4+5	COMP 6+7	COMP 8+9
Type	Pre	Pre	Pre	Pre	Pre	Post	Post	Post	Post	Post	Pre	Post	Post
Date	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13	16-09-13
Physical Tests													
% Moisture	15.3	15.2	15.0	16.0	15.2	14.6	14.8	14.5	14.7	15.2	-	-	-
% Sand	-	-	-	-	-	-	-	-	-	-	47.4	49.0	51.0
% Silt	-	-	-	-	-	-	-	-	-	-	28.5	28.4	26.8
% Clay	-	-	-	-	-	-	-	-	-	-	24.0	22.6	22.3
Texture	-	-	-	-	-	-	-	-	-	-	Loam	Loam	Loam / Sandy clay loam
Organic / Inorganic Carbon													
CaCO ₃ (%)	-	-	-	-	-	-	-	-	-	-	2.00	1.73	1.82
FOC (g/g)	-	-	-	-	-	-	-	-	-	-	0.0051	0.0048	0.0048
Inorganic Carbon (%)	-	-	-	-	-	-	-	-	-	-	0.24	0.21	0.22
Total Carbon (%)	-	-	-	-	-	-	-	-	-	-	0.7	0.7	0.7
Total Organic Carbon (%)	-	-	-	-	-	-	-	-	-	-	0.51	0.48	0.48
Petroleum Hydrocarbons (mg/kg)													
Benzene	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	-	-	-
Toluene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-	-	-
Ethylbenzene	0.513	<0.015	0.071	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	0.074	-	-	-
Xylenes	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-
Styrene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-	-	-
PHC F1 (mg/kg)	897	123	255	146	83	60	72	97	101	594	-	-	-
PHC F1-BTEX (mg/kg)	896	123	255	146	83	60	72	97	101	594	-	-	-
PHC F2 (mg/kg)	44	<20	22	<20	26	<20	<20	<20	<20	25	-	-	-
PHC F3 (mg/kg)	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-	-
PHC F4 (mg/kg)	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	-	-	-

Sample	CLOSE	10M	CONTROL
Date	16-SEP-13	16-SEP-13	16-SEP-13
Benzene ($\mu\text{g}/\text{m}^3$)	0.64	<0.64	<0.64
Ethylbenzene ($\mu\text{g}/\text{m}^3$)	1.17	<0.87	<0.87
Toluene ($\mu\text{g}/\text{m}^3$)	1.24	<0.75	<0.75
o-xylene ($\mu\text{g}/\text{m}^3$)	3.21	<0.87	<0.87
m+p-xylenes ($\mu\text{g}/\text{m}^3$)	12.4	<1.7	<1.7
Xylenes (Total) ($\mu\text{g}/\text{m}^3$)	15.7	<2.6	<2.6
PHC F1 ($\mu\text{g}/\text{m}^3$)	651	574	28
PHC F1-BTEX ($\mu\text{g}/\text{m}^3$)	632	574	28
PHC F2 ($\mu\text{g}/\text{m}^3$)	210	204	<15

DATA EVALUATION

The soil data were used to estimate the mass of contaminants lost to the atmosphere during the 1-hour remediation period. This data was incorporated into the previously developed Meridian emission model (2010) and emission outputs were compared to measured air concentrations obtained from the source and downwind air sampling location. Model inputs and outputs are included as Tables 3 and 4, respectively.

Parameter	Value
Contaminant thickness (m)	2
Source length (m)	20
Contaminated area (m^2)	400
Ethylbenzene - Maximum Initial Concentration (mg/kg)	0.513
Ethylbenzene - Average Initial Concentration (mg/kg)	0.12
Ethylbenzene - Average Final Concentration (mg/kg)	0.0148
PHC F1 - Maximum Initial Concentration (mg/kg)	897
PHC F1 - Average Initial Concentration (mg/kg)	310
PHC F1 - Average Final Concentration (mg/kg)	185
PHC F2 - Maximum Initial Concentration (mg/kg)	44
PHC F2 - Average Initial Concentration (mg/kg)	31
PHC F2 - Average Final Concentration (mg/kg)	5

Concentrations of parameters below laboratory detection limits (benzene, toluene, xylenes) were included in the model comparison using one half of the laboratory detection limit.

Table 4 Model Output Values	
Category	Ex-Situ Treatment
Short-term Exposure Concentrations ($\mu\text{g}/\text{m}^3$)	
Ethylbenzene	73
PHC F1	100,000
PHC F2	5,700
Long-term Exposure Concentrations ($\mu\text{g}/\text{m}^3$)^a	
Ethylbenzene	18
PHC F1	45,000
PHC F2	4,500

a – Day 5 average 8-hour concentration

MODEL COMPARISON

Compared to the measured vapour concentrations, the model significantly overpredicted PHC concentrations from *ex-situ* remediation. The predicted long-term exposure concentration of ethylbenzene ($18 \mu\text{g}/\text{m}^3$) was also overpredicted by a factor of 15 compared to measured concentration ($1.17 \mu\text{g}/\text{m}^3$), and the overall PHC concentration measured in vapour ($861 \mu\text{g}/\text{m}^3$) was more than 50 times lower than the predicted long term exposure concentrations ($49,500 \mu\text{g}/\text{m}^3$).

CONCLUSIONS

Predicted volatile PHC exposure concentrations were significantly overpredicted and may be overly conservative. Based on the available data, the allu (TM) treatment method appears to be protective of nearby air quality and emissions result in concentrations that are lower than regulatory guidelines by at least an order of magnitude.

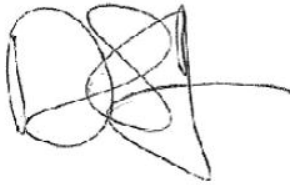
CLOSURE

We thank you for the opportunity to be of assistance to the Petroleum Technology Alliance of Canada. Should you have any questions, please contact either of the undersigned at 403-270-4724.

Yours truly,

Millennium EMS Solutions Ltd.

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