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Evaluation of Contaminant Migration and Remedial Goals for A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit Trenches Area (U)

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EXECUTIVE SUMMARY

The trenches area of the A-Area Miscellaneous Rumble Pile contained volatile organic compounds that posed a migration threat to groundwater. Predicted concentrations from a 2000 model for trichloroethylene and tetrachloroethylene exceeded Maximum Concentration Levels in ground water. These predicted exceedances led to the establishment of remedial goals for the unit and the installation of a soil vapor extraction (SVE) system. The system, which recently transitioned from active to passive, has shown diminishing removals and low soil vapor concentrations, in agreement with a depletion of contaminant source in the vadose zone. To determine location and quantity of residual mass of contaminants, the source zone ash and underlying soil was recently sampled, in turn establishing depth profiles and providing input into an updated contaminant migration model for the unit. The updated model, completed in 2019, concluded that the residual source no longer poses a migration threat to groundwater. The considerable difference in predicted contaminant impact on groundwater between the 2000 and 2019 models warranted further assessment of the most important parameters and assumptions. This critical analysis of the contaminant depth profiles and the main assumptions of the 2019 model suggests that the SVE system will largely be ineffective in removing the immobile and diffusion rate controlled residual mass in the ash layer. This detailed understanding of the source unit and thorough analysis of sensitive model parameters supports the shutdown of the passive soil vapor extraction system.

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ARP	A-Area Miscellaneous Rubble Pile
ASVE	Active Soil Vapor Extraction
ft	feet
f_{oc}	fractional organic content
g	grams
in	inches
K_d	Soil-water partition/sorption coefficient
kg	kilograms
K_{oc}	organic-carbon partition coefficient
L	liters
MCL	maximum contaminant level
mg	milligrams
OU	Operable Unit
PAH	Polycyclic aromatic hydrocarbon
PCE	tetrachloroethylene
RG	Remedial Goal
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
SVE	soil vapor extraction
TCE	trichloroethylene
VOC	volatile organic compound
VZCOMML	Vadose Zone Contaminant Migration Model Multi Layered

1.0 INTRODUCTION

In 2019, the nearly 20-year old fate and transport model utilized for the trenches area at the A-Area Miscellaneous Rubble Pile (ARP) Operable Unit was updated using characterization data gathered in 2018. The updated model demonstrated that ARP did not pose a threat to groundwater at current source zone concentrations, though these concentrations have not met current remedial goals (RGs). Such conclusions indicate that current RGs, which are based on the previous model, may need to be updated. This white paper evaluates the potential future impact of volatile organic compounds (VOCs) in the ARP on ground water and the current RGs established in the *Record of Decision Remedial Alternative Selection for the A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit* (WSRC, 2003). This evaluation includes: background information on the ARP; an examination of the results of 2018 sampling effort; a discussion of current VOC vapor concentrations; an evaluation of the recent modeling effort with analysis of select key parameters; and a recommendation on the feasibility and appropriateness of reaching established RGs.

2.0 ARP

The ARP (731-6A) Operable Unit (OU) is listed as a Resource Conservation and Recovery Act 3004(u) Solid Waste Management Unit/Comprehensive Environmental Response, Compensation, and Liability Act Unit in Appendix C of the Federal Facility Agreement for the Savannah River Site (SRS).

The ARP OU is located in the northwest portion of the SRS within A Area and immediately east of M Area. It is approximately 1.1 miles from the nearest site boundary. The unit covers 5.8 acres and is bounded on the southwest and southeast by outfall drainages that coalesce on the south side of the unit (Figure 1).

The ARP OU has been divided into three subunits: The Piles Area, the Ash Area, and the Trenches Area (Figure 1). The Piles Area (2.3 ac) contains many small mounds (2- to 5-feet high) of construction debris that were disposed of directly on the ground surface. The Ash Area (1.8 ac) contains buried construction debris and an ash layer of 4 ft. The Trenches Area (1.6 ac) contains construction debris in an 8- to 12-ft deep T-shaped trench.

Of the three units, only contaminants in the Trenches Area posed a threat to groundwater where leaching of trichloroethylene (TCE) and tetrachloroethylene (PCE) could lead to groundwater concentrations above their respective maximum contaminant levels (MCLs) of 5 µg/L. Soil RGs of 0.0877 and 0.656 mg/kg for TCE and PCE, respectively, were established to prevent such exceedances. The remedial actions for the trenches area to date consist of three components: a 1-ft soil cover, an active soil vapor extraction (ASVE) system, and institutional controls. The soil cover was installed between October and December 2003. Operation of the ASVE system commenced on April 26, 2004. SRS transitioned from ASVE to passive SVE in 2017 with a combination of MicroBlowers™ and BaroBalls™ placed on seven SVE wells and on twelve former vapor monitoring wells. Annual vapor concentrations of PCE and TCE are measured to determine mass removed which is reported in a yearly Performance Evaluation Report.

Additional characterization of the ash layer and vadose zone soils located beneath the Trenches Area soil cover was conducted in July 2018 (SRNS, 2018a). As defined in the Sampling Analysis Plan (SRNS, 2015), this effort was to evaluate if the VOCs are partitioned in the hydraulic/cutting oils and to provide information on the remaining VOC concentration in soil and ash.

2.1 2018 Sampling Effort

The 2018 sampling effort (SRNS, 2018a) collected samples of ash and underlying soils at 14 locations (Figure 2) throughout the ARP trenches area to determine the concentrations and depth profiles of VOCs and hydraulic/diesel fluid for use in contaminant fate and transport modeling. The sampling effort also aimed to determine whether the VOC contamination is correlated with ash and/or the hydraulic fluids. Soil samples beneath the ash were unable to be obtained at two locations due to auger refusal at AMRP15TR-05 and the possible presence of asbestos at AMRP15TR-14. The maximum sample concentrations (4.17 mg/kg for TCE and 4.39 mg/kg for PCE) were used in the recent refinement of the contaminant fate and transport model for ARP (see SRNS, 2018b - with further discussion in section 3.0).

Based on where ash was encountered during the 2018 sampling effort, the layer of clean soil (including the one-foot cap) on ARP is generally 4 to 6 ft thick. The ash extends 12 to 15 ft below ground surface, resulting in a 6 to 10 ft thick ash source layer. VOC contamination was mostly confined to the ash layer as soil samples beneath the source zone had VOC concentrations distinctly lower than the ash above (Figures 3 & 4). Concentrations of both TCE and PCE were less than that of the ash above at 10 of the 12 locations where soil samples were taken with order of magnitude decease in concentrations for 7 of the 10 locations (7 of 12 overall), though most of these locations still exceed the RGs (33 and 29 of 53 sample points exceed for TCE and PCE, respectively). The differences in concentrations between the ash and underlying soils suggests that there is little migration of contamination from the source layer.

To evaluate the correlation of constituent concentrations, a correlation coefficient between both VOC concentrations and hydraulic/diesel concentrations was calculated at each sample location. Correlation coefficients, determined in Excel, range from -1 to 1, with values closer to 1 quantitatively indicating a strong positive correlation and values closer to -1 a strong negative correlation. A value of zero indicates the datasets are not correlated. The VOC concentrations were not correlated with concentrations of hydraulic/diesel fluids as values ranged from -0.96 to 0.94 for TCE and -1 to 0.94 for PCE (Table 1). The average values were not significantly different than zero, signifying no correlation between the VOC and hydraulic fluid concentrations. The lack of a correlation between the concentrations of VOCs and hydraulic/diesel fluids indicates that the strong retention of VOCs in the source zone is not from the presence of hydraulic/diesel fluids but likely from the organic content of the ash itself (see discussion in section 3.1).

2.2 Current Vapor Concentrations

Soil vapor concentrations of both TCE and PCE have consistently decreased over the past 15 years (Figure 5). Low concentrations in recent years suggest that minimal mass is available to the SVE unit (i.e. sorbed to ash or located in low permeability zones). Thus, the mobile VOCs have seemingly been removed by the SVE system, leaving behind only diffusion rate controlled contamination that will be unaffected by continued use of the system. The immobile VOCs in the source zone are likely adhered to ash with a high organic content or within low permeability areas.

The consistent decrease of VOC soil vapor concentrations also indicates that the reduction in flow rates as the system was transitioned from active to passive in 2017 did not result in an increase in vapor concentrations. Rebounds in VOC concentrations are possible after an alteration to an SVE system if the vadose zone still contains sufficient available mass of contaminant. The lack of a rebound supports the conclusion that the available mass of VOCs in the vadose zone is minimal.

2.3 RG Evaluation

Current maximum (4.17 mg/kg for TCE and 4.39 mg/kg for PCE) and average concentions VOC concentrations in (0.77 mg/kg for TCE and 1.22 mg/kg for PCE) in the source zone are significantly higher than the established soil RGs of 0.0877 and 0.656 mg/kg for TCE and PCE, respectively. However, the diminishing soil vapor concentration for both VOCs and the source zone depth profiles indicate that there is little mass available to the SVE system in the source zone, making the achievement of RGs through SVE unlikely. To address the potential threat that the residual VOC contamination in the source zone poses to groundwater, an update of the contaminant migration model for ARP.

3.0 GROUNDWATER MODEL EVALUATION

The 2019 refinement of the fate and transport model was performed with the VZCOMML spreadsheet model (SRNS, 2019) and included the consideration of four primary factors. First, active and passive SVE have removed VOC mass and reduced PCE and TCE concentrations in the vadose zone. Second, the updated fate and transport model included a greater level of discretization (five layers instead of two) based on recent lithology characterization and incorporates site specific data that account for thin layers of low hydraulic conductivity material beneath the source. The increased numerical detail and stratigraphy refinement result in longer travel times and increased attenuation of constituents. Third, a lower water table elevation was used based on more recent water table data, creating a greater vadose zone transport distance resulting in longer travel times and increased attenuation of contaminants. Finally, the new model considered degradation from various sources (biological, hydrolysis, etc.) of TCE and PCE in the source and vadose zones, a factor not considered in the original model (WSRC, 2000).

The refined model results indicated that constituents in the source zone of ARP are not a migration threat to groundwater and predicted groundwater concentrations that were orders of magnitude below MCLs, supporting the discontinuation of the SVE system. As part of the modeling effort, a sensitivity analysis was performed to establish the parameters that most influenced the model results. The top five parameters based on relative sensitivity of TCE and PCE concentrations in groundwater were:

1) faction organic contents in the source zone (f_{oc})

2) infiltration rate through the vadose zone

3) retardation coefficient

4) degradation half-life

5) mixing zone thickness

These parameters were discussed within the report, however a more thorough commentary with emphasis on these most influential parameters is warranted considering the importance of the final conclusions. The level of conservatism for each parameter was analyzed for the level of conservatism using field observations and literature values.

3.1 Fraction of Organic Content and Retardation Coefficient

The results of the model were sensitive to both the retardation coefficient and the fraction of organic carbon. Retardation coefficients (*R*, equation 1) are largely dependent on the sorption coefficient (K_d), which in turn is estimated for TCE and PCE (equation 2) using the fraction organic content (f_{oc}) and the organic carbon partitioning coefficient for each compound (K_{oc}).

$$R = 1 + \frac{\rho_b}{n_e} K_d \qquad (1)$$

Where:

ρ_b is the porous media bulk density, and

ne is the effective porosity of the media

$$K_d = f_{oc} \times K_{oc} \qquad (2)$$

Since the K_{oc}, ρ_b, and *ne* are all well-established parameters with a small range of possible values relative to f_{oc}, the f_{oc} is the main driver for the observed sensitivity. In the 2019 model, the value for f_{oc} is 0.00266 which assumes the ash source layer has a low organic content similar to clean aquifer sand. This value is quite conservative considering coal fly and bottom ash is known to have a f_{oc} ranging from 0.017 to 0.1 (Riberiro 2014, Singh 2009) making the modeled value at least an order of magnitude below the those found in the literature. Further, the high retention of TCE and PCE in the source zone, in absence of a correlation between VOC and hydraulic fluid concentrations, indicates a high affinity of the VOCs for ash, supporting a higher f_{oc} in the source layer. Finally, in the original sampling effort (WSRC, 2000), a TOC concentration of 52,750 mg/kg was found in the source zone equating to a f_{oc} of 0.05. As such the modeled value of f_{oc} is concluded to be very conservative and likely over an order of magnitude low compared to field results and literature values.

3.2 Infiltration Rate Through the Vadose Zone

Infiltration rate though the vadose zone, or percolation, is a factor of both the infiltration rate into the subsurface and the vadose zone permeability/porosity. The average annual infiltration into the surface for A/M area is 17 in. per year which is calculated by taking an annual rainfall of 48 in. (measured in 1991 at the Savannah River Technology Center gauging station in the A/M Area) less 31 in. of evapotranspiration based on the site average of 64% loss. At ARP this infiltration is slowed by the clayey sediments beneath the trenches and the infiltration rate through the vadose zone is estimated at 3.2 in/yr, the value used in the 2019 model. This value was determined in the original modeling effort (WSRC, 2000), which was previously compared to field conditions including moisture content, bulk density and hydraulic conductivity (SRNS, 2018b). Sensitivity analysis reveals the infiltration rate through the vadose zone would need to be increased to 1.7 ft/yr (20.4 in/yr) for predicted concentrations to exceed MCLs, which is greater than the overall infiltration rate for A/M area. As such, the modeled value of infiltration rate through the vadose zone is concluded to be representative of site-specific field conditions and are not conservative.

3.3 Degradation Half-life

A degradation half-life of 10 years was used for both TCE and PCE in the 2019 model, while degradation was not considered in the 2000 version. Currently, a comparison to field conditions for degradation half-life is not possible due to the differences in sampling design between 2000 and 2019. In 2000, samples were randomly taken to establish if contamination was present while the targeted sample plan in 2018 aimed to capture the zones containing the highest contaminant concentrations. These data sets cannot be quantitatively compared due to the introduced skew arising the preferential sampling in 2018, necessitating the use of literature values in the model. The modeled half-lives were default values to the VZCOMML spreadsheet model which was developed to model the vadose zone at SRS. The half-lives in the default model are based on published values of ~1 year (Howard et al, 1991) with an order of magnitude safety factor (Rucker, 2011). Sensitivity analysis revealed that the half-lives would need to be increased to 80 years for predicted concentrations in groundwater to exceed MCLs (SRNS, 2018b). As such, the half-lives used are seemingly conservative but are without field comparison.

3.4 Mixing Zone Thickness

Within the 2019 model, the mixing zone defines the aquifer area underneath the unit where contaminants are mixed. The mixing zone was defined from the water table to the local green clay confining unit (16.5 ft) in the Upper Lost Lake aquifer zone. The green clay is a poor confining unit and allows some vertical transport between M-Area aquifer and the Lost Lake aquifer, which is about 50 feet thick. Therefore, the use of the green clay as a confining unit and, as a result, the 16.5-foot thickness of the mixing zone is conservative. It should be noted the both the M-area and Lost Lake aquifers are contaminated in area due to releases not associated with ARP.

4.0 CONCLUSIONS/RECOMMENDATIONS

The contaminant migration model results for ARP were most sensitive to f_{oc}, for which a very conservative value was used. *The other sensitive parameters included* less conservative values (half-life, infiltration) and conservative (source depletion, mixing zone thickness) values. This assessment supports the conclusion that the residual VOC source in the ash poses no threat to groundwater and predicted concentrations will remain below the respective MCLs for PCE and TCE. Further, due to the confinement of the residual source in the ash, soil vapor concentrations are diminishing with no evidence of a rebound after the switch from ASVE to passive SVE. In conjunction with the results of the updated migration model, field conditions and observations support the shutdown and removal of the passive SVE system. Should a change to the RG value be regulatorily required to support closure, the updated transport model can be used to develop the revised RGs. Alternatively, the existing wells could be operated as barometric pumping wells only, reducing maintenance cost while still removing diffusion rate-controlled VOCs from the trench.

5.0 REFERENCES

Howard, P.H. et al., 1991. Handbook of Environmental Degradation Rates, Lewis Publishers

Ribeiro et al, 2014. Fly ash from coal combustion – An environmental source of organic compounds, Applied Geochemistry, Vol 44, 103-110.

Rucker, Gregory, G., 2011. Soil Contaminant Migration Screen Software Calculation Check (U) for VZCOMML v. 4.0, Q-CLC-G-00089, Revision 0, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.

Singh, N., 2009. Adsorption of herbicides on coal fly ash from aqueous solutions, Journal of Hazardous Materials, Vol 168, Issue 1, 233-237.

SRNS, 2015. Sampling and Analysis Plan for the A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit (U), SRNS-RP-2015-00007, Revision 1, Savannah River Nuclear Solutions, Savannah River Site, Aiken SC

SRNS, 2018a. Post-Construction Report Addendum for the A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit (U), SRNS-RP-2018-00942, Revision 0, Savannah River Nuclear Solutions, Savannah River Site, Aiken SC

SRNS, 2018b. Contaminant Migration Model for the A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit (U), SRNS-RP-2018-01190, Revision 0, Tetra Tech, Inc., Alpharetta GA

WSRC, 2000. Resource Conservation and Recovery Act (RCRA) Facility Investigation/ Remedial Investigation with Baseline Risk Assessment for the A-Area Miscellaneous Rubble Pile (731-6A) (U), WSRC-RP-98-4208, Revision 1, Westinghouse Savannah River Company, Savannah River Site, Aiken SC

WSRC, 2003. Record of Decision Remedial Alternative Selection for the A-Area Miscellaneous Rubble Pile (731-6A) Operable Unit (U), WSRC-RP-2001-4197, Revision 1.3, Westinghouse Savannah River Company LLC, Savannah River Site, Aiken, SC

Table 1. Correlation coefficients between constituent concentrations at each sample location. Location AMRP15TR-16 only had 2 data points making the correlation coefficient meaningless. AMRP15TR-07 and AMRP15TR-10 were not sampled due to auger refusal.

	Correlation Coefficient		
Location	TCE : Diesel	PCE : Diesel	TCE : PCE
AMRP15TR-01	0.40	0.48	0.98
AMRP15TR-02	-0.96	-0.97	1.00
AMRP15TR-03	0.31	0.65	0.92
AMRP15TR-04	-0.96	-0.97	1.00
AMRP15TR-05	0.94	0.96	1.00
AMRP15TR-06	-0.96	-0.97	1.00
AMRP15TR-07	Not sampled		
AMRP15TR-08	-0.66	-0.70	0.98
AMRP15TR-09	-0.96	-0.97	1.00
AMRP15TR-10	Not sampled		
AMRP15TR-11	0.42	0.00	0.91
AMRP15TR-12	-0.85	-0.77	0.41
AMRP15TR-13	0.64	0.74	0.97
AMRP15TR-14	-0.95	-1.00	0.95
AMRP15TR-15	-0.95	-1.00	0.95
AMRP15TR-16	Insufficient data		
Average	-0.35	-0.35	0.93
Standard Dev.	0.70	0.73	0.15

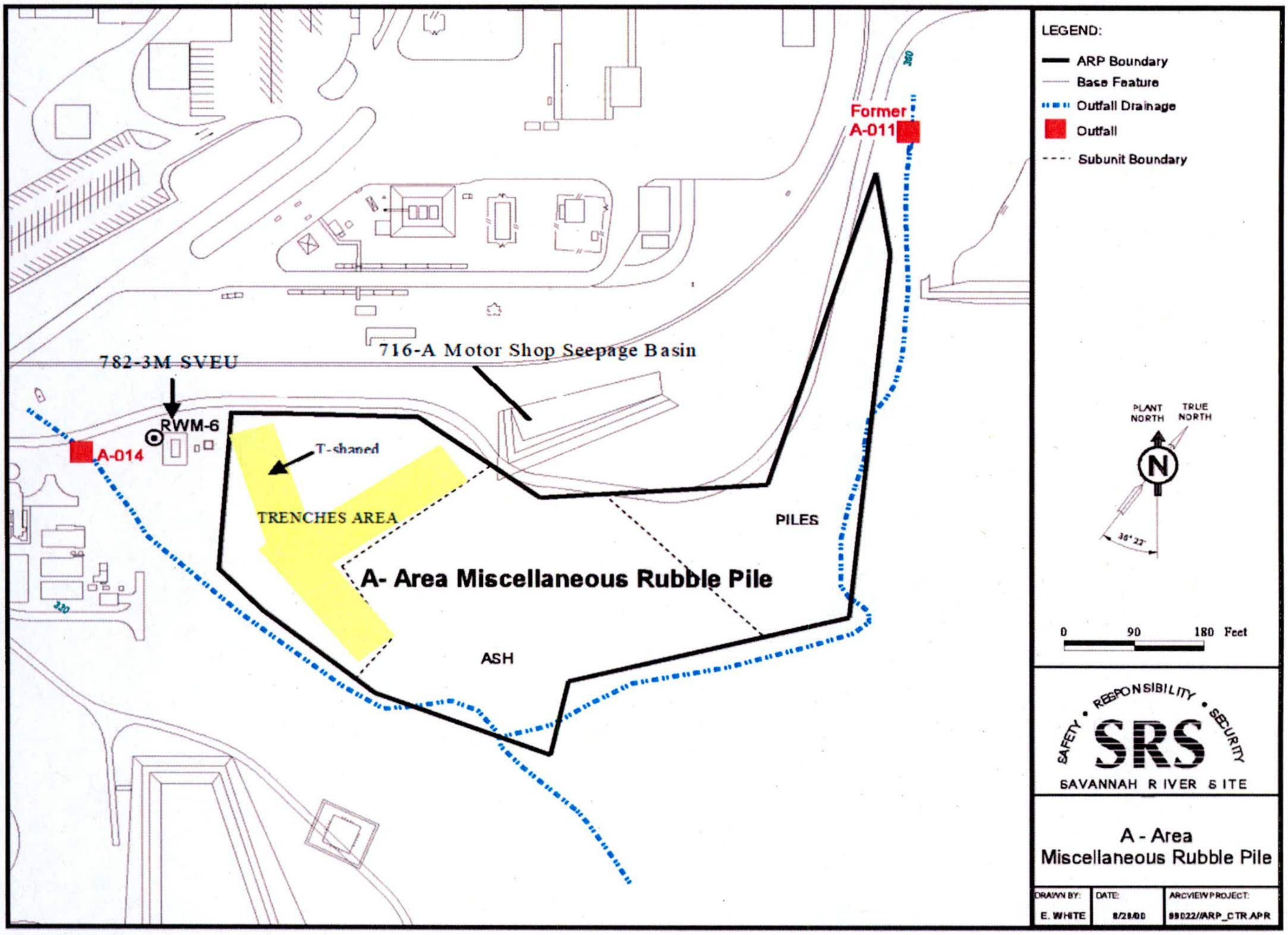

Figure 1. ARP OU (731-6A)

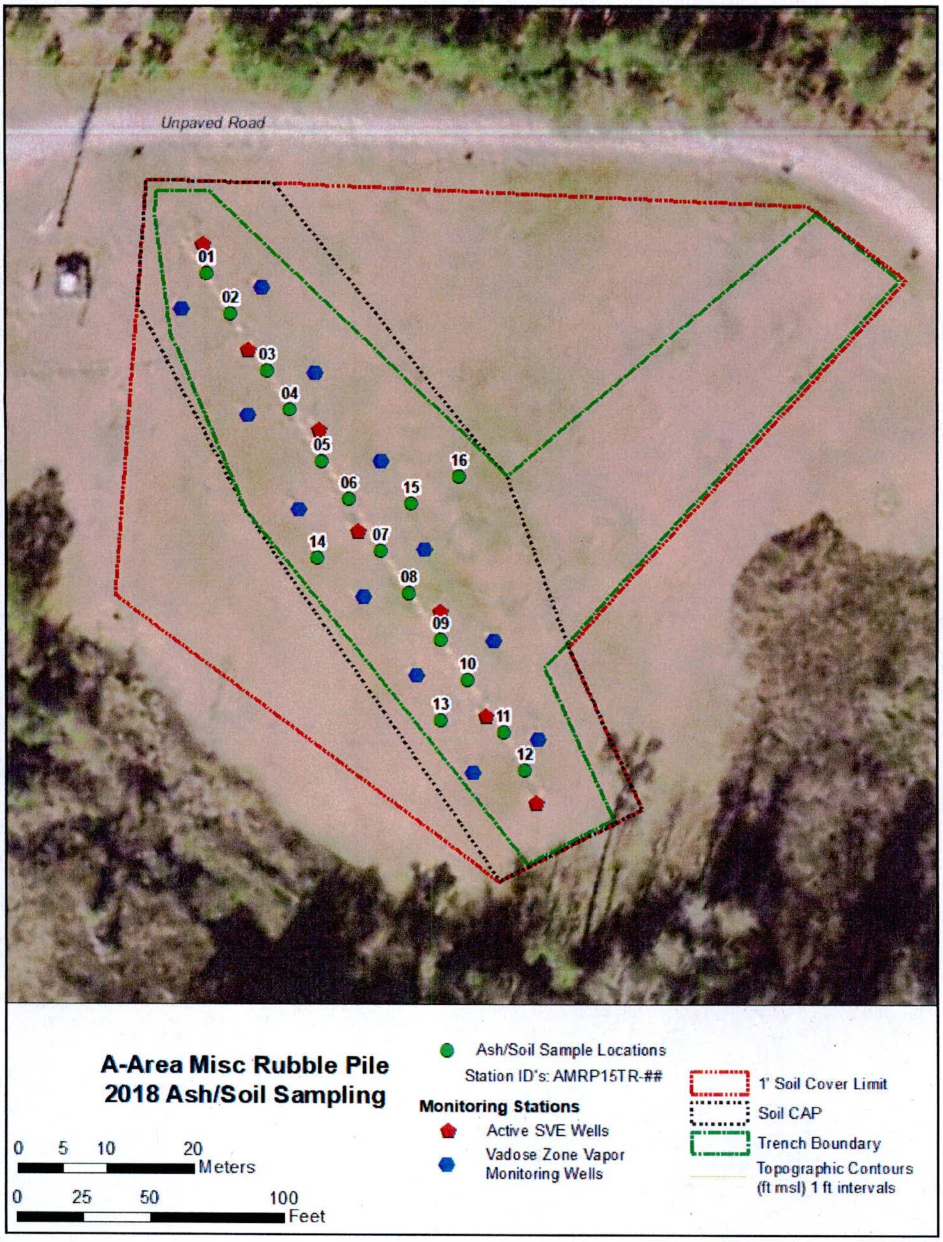

Figure 2. 2018 ARP sampling locations

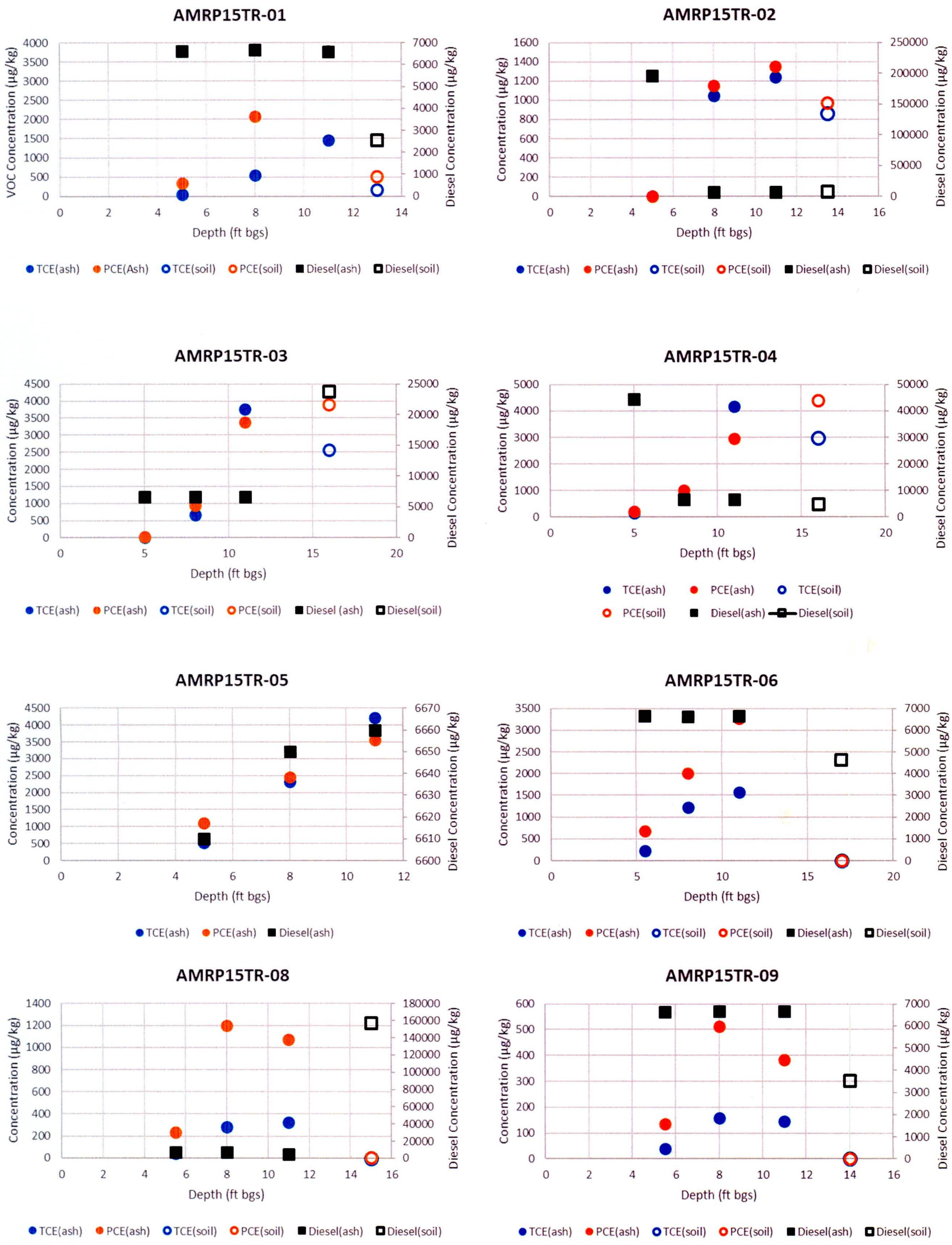

Figure 3. **TCE and PCE concentrations in ash and soil samples during 2018 ARP sampling effort – locations 1-9***

*AMRP15TR-07 was not sampled due to auger refusal.

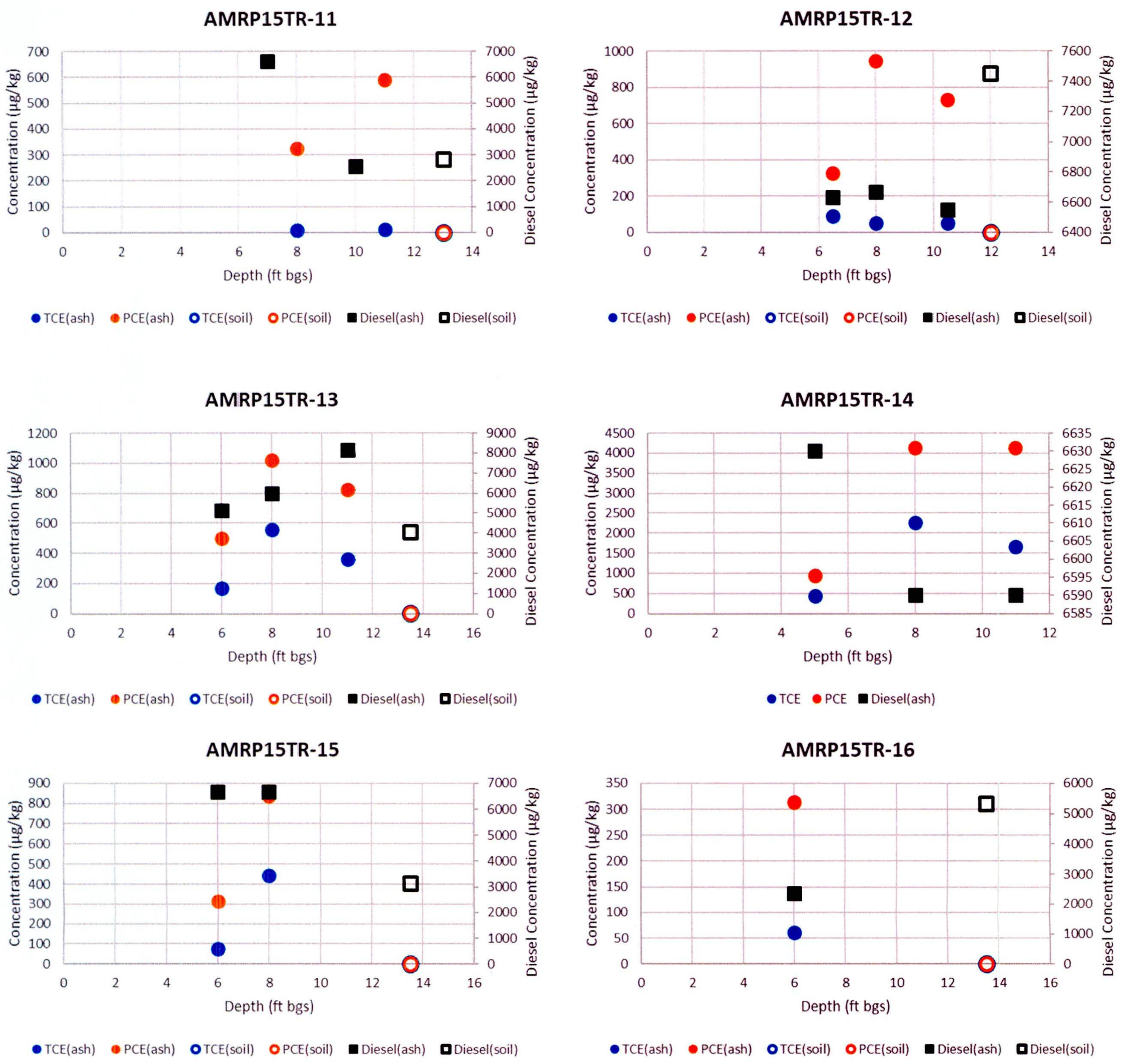

Figure 4. TCE and PCE concentrations in ash and soil samples during 2018 ARP sampling effort – locations 11-16*

*AMRP15TR-10 was not sampled due to auger refusal.

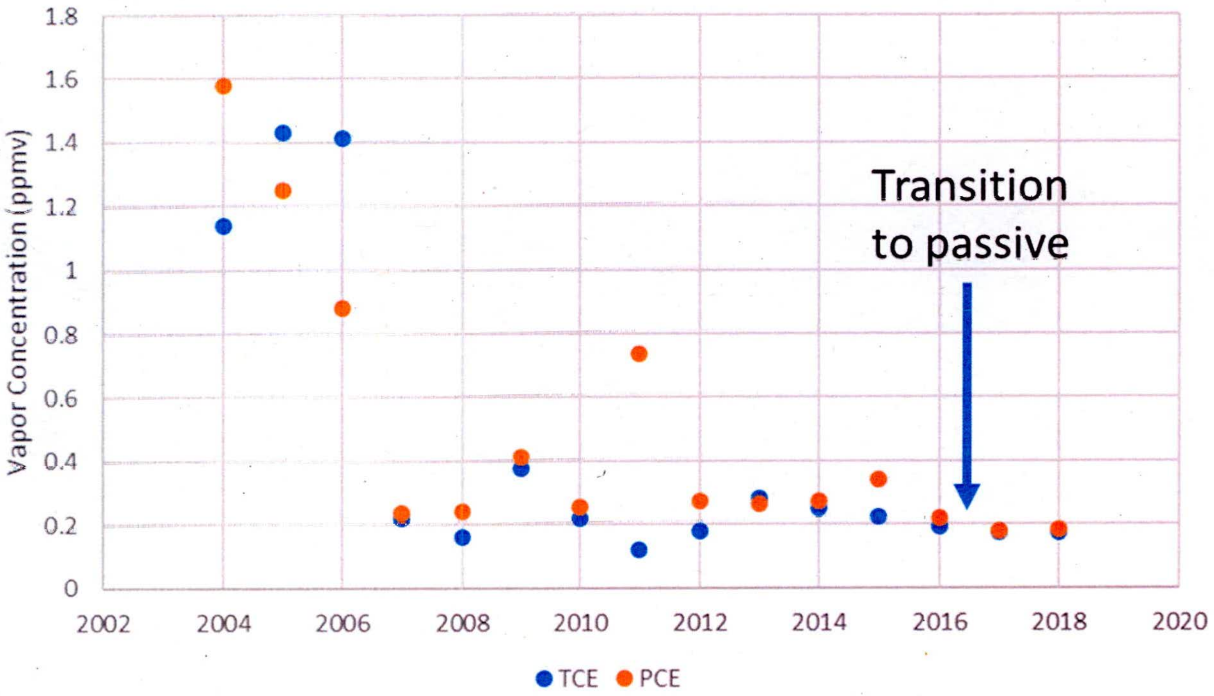

Figure 5. Average vapor concentrations of TCE and PCE in all extraction wells