

Option	Description	Implementability		Comments
		Potential Advantages	Potential Disadvantages	
Management Options All Systems				
No Action	Restart the system and dispose spent Granular Activated Carbon (GAC) as mixed low level radioactive waste (LLRW).	<ul style="list-style-type: none"> Limited regulatory approval required. Treatment operations could resume immediately, upon system re-commissioning. 	<ul style="list-style-type: none"> High disposal cost, approximately \$10,000 per 55-gallon drum. 	
Increased Frequency of GAC Exchange	<p>Demonstrate F-listing is not appropriate; restart the systems; increase exchange frequency so that VOCs are below RCRA or Land Disposal Requirement (LDR) limits; and, dispose GAC as non-hazardous LLRW at Nevada Test Site, Energy Solutions - Clive, or other facility.</p> <p>Obtain authorization to inject ground water back into the subsurface for final disposition of tritiated water. The design, permitting, and installation of injection wells for TF518-N are required.</p>	<ul style="list-style-type: none"> Eliminates mixed waste and related disposal cost. Limited regulatory approval required. Multiple potential disposal sites available. Short resumption time frame. 	<ul style="list-style-type: none"> More frequent GAC change out, creating higher O&M labor costs. Risk associated with improper characterization resulting in hazardous waste discharge. Increased GAC disposal is contrary to LLNL waste minimization objectives. Spent GAC may still be hazardous by EPA's toxicity criteria. 	<ul style="list-style-type: none"> This option requires thorough understanding/prediction of the liquid and vapor phase adsorption isotherm and design. An appropriate and validated adsorption model is required to predicted GAC change out frequency. A Standard Operating Procedure (SOP) is required for waste profiling, e.g. frequency of sampling, sample and analytical methods, etc. Spent GAC from TF518-N will be evaluated against toxicity criteria in 40 CFR 261.24 to determine if it is hazardous waste. Spent GAC may still be mixed waste if chemical concentrations exceed toxicity characteristic leaching protocol (TCLP) limits. Permitting changes for TF518-N would be required with a minimum of an Explanation of Significant Difference (ESD).
Authorized Limit	Obtain an Authorized Limit per DOE Order 5400.5; restart the systems; and dispose spent GAC at a permitted RCRA treatment facility waste.	<ul style="list-style-type: none"> Eliminates mixed waste handling problems. A technical basis for an authorized limit was established in 2007 for a specific facility in Texas. Cost savings associated with disposal of material with an Authorized Limit. 	<ul style="list-style-type: none"> DOE / NRC approval required. Requires a treatment storage and disposal facility willing to participate in the authorized limit process. A long time period may be required to obtain the authorized limit. Low volume of mixed waste (30 drums/year) may not provide economic incentive for disposal facility to take on increased regulatory compliance requirements. Technical basis for Authorized Limit has inherent assumptions for risk calculations. The assumptions will become operational restrictions on how the spent GAC is handled. A detailed risk analysis will need to be performed for the treatment facility receiving the GAC. 	<ul style="list-style-type: none"> Per DOE Order 5400.5, an Authorized Limit will result in an annual public dose of 100 milliroentgen-equivalent man per year (mrem/year) or less. A technical basis for Authorized Limits of 4,400 pCi/g for tritium, 1,100 pCi/g for lead-210, bismuth-210 and polonium was proposed by Weiss Associates in 2007 in accordance with DOE Order 5400.5. The RCRA treatment facility LLNL contacted during the Authorized Limit study, the Clean Harbors Deer Park TX facility, elected not to participate in further negotiations with LLNL as they would have potentially had to modify their regulatory permits. This was the procedure used at the Hanford Site for a similar GAC mixed waste problem.

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Preliminary List of Alternatives for Treatment Facilities
 TF5475-1, TF5475-3, VTF5475, and TF518 North
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Plume Control to Exclude Tritium (HTO) from Wells Used for VOC Treatment	Install additional hydraulic control with new wells or increased pumping at existing wells to prevent migration of tritium into the areas where pumping is being conducted for VOC treatment.	<ul style="list-style-type: none"> Eliminates the potential production of mixed waste in the VOC treatment facility. 	<ul style="list-style-type: none"> Hydrogeologic feasibility not established. Additional cost associated with new pumping configuration. TF518-N source study needed. 	<ul style="list-style-type: none"> Assumes no HTO source in VOC area. A similar alternative would be to control and treat the chlorinated hydrocarbon plume by pumping from areas that do not contain tritium.
GAC Flushing	<p>At each treatment system, flush spent GAC with clean water to remove HTO; inject the flush water back into the subsurface; and, dispose spent GAC as RCRA waste.</p> <p>Approximately 4 to 5 GAC pore volumes of clean water are necessary to reduce HTO to less than 100 pCi/L (LLNL, 2009).</p>	<ul style="list-style-type: none"> Eliminates mixed waste in the GAC. Relatively simple technology. Can be used for mixed waste generated from both aqueous and vapor processes. 	<ul style="list-style-type: none"> Flush water is a new LLRW waste stream requiring disposal. Flushing may desorb VOCs from GAC, which would require that the flush water be passed through the new GAC filter before injection into the subsurface. Risk associated with improper characterization resulting in LLRW discharge. Additional bench and pilot scale tests and associated costs required. 	<ul style="list-style-type: none"> The proof of concept study performed at LLNL did not include HTO analysis of the GAC matrix and does not evaluate potential for flushing to desorb VOCs. Feasibility of injecting potentially large volume of water (permitting, hydrogeology, etc.) needs to be evaluated.
Onsite Regeneration of GAC	<p>Obtain modification to LLNL RCRA Part B permit; design and install an onsite facility to regenerate GAC.</p> <p>Typically, GAC is regenerated thermally in a rotary kiln or multiple hearth furnace.</p>	<ul style="list-style-type: none"> No offsite shipment of waste. 	<ul style="list-style-type: none"> Relatively complex treatment process with high O&M requirement. Multiple new waste streams. Permitting challenges. High cost relative to other options, particularly high capital costs. 	<ul style="list-style-type: none"> Currently no such GAC regeneration facility exists at LLNL. Preliminary analysis indicates that this alternative does not likely warrant further evaluation.
Modification to Existing Aqueous Process TF5475-1, TF5475-3, and TF518 North				
Catalytic Reductive Dehalogenation (CRD) Process Modification	Use a different catalyst, such as platinum or other alloy, in the same process to more efficiently reduce the chlorinated hydrocarbons. Adjust operational parameters (such as temperature or pH) to increase the effectiveness of the existing CRD system.	<ul style="list-style-type: none"> Easy to implement. Eliminates mixed waste generation. Keeps the same strategy in place. No additional permitting required. Technology destroys VOCs, 	<ul style="list-style-type: none"> Platinum cost is four times that of palladium. O&M issues remain. High energy consumption for temperature increase, which may also require added protections. Currently unable to achieve 90% destruction efficiency. 	<ul style="list-style-type: none"> LLNL experience with this process could help in upgrading or redesigning the system. The technology has been demonstrated; reliable operations have not been achieved. As a variation of this idea, perhaps a lower efficiency in reduction of VOCs could be permitted by the regulatory agencies to make the existing system or its modification acceptable.
Revise CRD performance criteria to less than 90% Total VOC destruction.	Remove GAC; restart existing CRD systems; revise performance criteria to an achievable level; operate at maximum treatment efficiency until HTO has decayed to an acceptable level; and then re-evaluate VOC treatment options.	<ul style="list-style-type: none"> Utilizes existing facilities. Removes GAC from the process. 	<ul style="list-style-type: none"> Operational issues with the CRD remain. Hydrogeology modeling may be required to confirm that <90% effectiveness will meet remediation objectives. 	<ul style="list-style-type: none"> Tests would need to be conducted to determine the achievable efficiencies.
New Aqueous Process TF5475-1, TF5475-3, and TF518 North				
Ex-situ UV/Chemical Oxidation	Oxidation of target contaminants by direct reaction with oxidizers, UV photolysis, and through the synergistic action of UV light, in combination with ozone (O ₃) and/or hydrogen peroxide (H ₂ O ₂).	<ul style="list-style-type: none"> No chlorinated hydrocarbon waste. Part of VOC remediation program. Technology destroys VOCs, 	<ul style="list-style-type: none"> Previous experience with oxidation using UV at LLNL required high operation and maintenance effort. Handling of hazardous material (H₂O₂) and high energy requirements 	<ul style="list-style-type: none"> Catalyst systems used to oxidize VOCs typically use metal oxides such as nickel oxide, copper oxide, manganese dioxide, or chromium oxide. Noble metals such as platinum and palladium may also be used. Most commercially available catalysts are proprietary. The thermal or catalytic oxidation process can be enhanced to reduce energy costs by using counter-flow heat exchangers to transfer heat from the exhaust stream to the incoming contaminated stream.

<p><i>Ex-situ</i> Reductive Dehalogenation</p>	<p>Reductive dehalogenation of chlorinated hydrocarbons using a reducing agent such as Ferrous (Fe²⁺) ion, zero-valent iron, or other reducing chemicals.</p>	<ul style="list-style-type: none"> • Easy to implement. • Eliminates mixed waste generation. • Keeps the same strategy in place. • No additional permitting required. 	<ul style="list-style-type: none"> • May not achieve high enough destruction rate of the halogenated hydrocarbons to meet the current requirement of at least 90% destruction. • Requires testing. 	<ul style="list-style-type: none"> • If excess chemicals are used in this <i>ex-situ</i> reaction, and the effluent is injected back into the formation, the excess reactants could continue to reduce the chlorinated hydrocarbons in the subsurface, providing some <i>in-situ</i> remediation in the subsurface. • Feasibility of combinations of metals were shown in “Development of a wastewater treatment process: Reductive dehalogenation of chlorinated hydrocarbons by metals,” Christian Schlimm, Ewald Heitz, Environmental Progress, Volume 15 Issue 1 (July 2006), Pages 38 - 47. • A variation of this concept is an electro-chemical reaction, in which the reduction reaction takes place at specifically designed cathodes, as described in “Reductive Dehalogenation of Aqueous-Phase Chlorinated Hydrocarbons in an Electrochemical Reactor,” by Jiahan He, Wendell P. Ela, Eric A. Betterton, Robert G. Arnold, and A. Eduardo Sáez, Ind. Eng. Chem. Res., 2004, 43 (25), pp 7965–7974.]
<p>Air Stripping</p>	<p>Treatment by contacting the water with a flow of air to transfer dissolved VOCs from the liquid phase to the vapor phase. To prevent release to the atmosphere, VOCs from the exhaust air stream are typically adsorbed by GAC, while the air is reinjected to the subsurface in a manner similar to the process used in VTF5475.</p>	<ul style="list-style-type: none"> • This is a proven technology for removal of VOCs from water. 	<ul style="list-style-type: none"> • The resulting VOC-containing air stream has to be treated similar to VTF5475. The air would be saturated with water containing tritium. See the discussion of VTF5475 below for possible options. 	<ul style="list-style-type: none"> • The operation of VTF5475 provides experience for handling the VOC-containing air stream. • High volume of air may be required to remove VOCs, which would cause high volume of air to be injected into the subsurface. • Air stripper exhaust may contain HTO.
<p>Modification to Existing Vapor Process VTF5475</p>				
<p>Hydrophobic Adsorption Media</p>	<p>Utilize water repellent adsorbing material to remove VOCs without the collection of tritiated water.</p>	<ul style="list-style-type: none"> • Avoids the generation of mixed waste. 	<ul style="list-style-type: none"> • Sufficient water or water vapor may be retained in the matrix to constitute a mixed waste. • Tests will need to be run to determine effectiveness of this option. • Not a proven technology for this application. 	<ul style="list-style-type: none"> • Potential hydrophobic absorption material: <ul style="list-style-type: none"> ○ Silica aerogel ○ Refined activated carbon (Sorbeum) [also absorbs chromium] ○ Cellulose absorbent (K-Sorb hydrophobic fiber and MOP) ○ Polyester foam (Sunsorb Orange Diamond Absorbent) ○ Di(2-ethylhexyl) adipate (DEHA) [liquid] ○ Processed Reba tree bark (ABTEK) ○ Polyolefins (3M) ○ Amphiphilic Urethane • Preliminary analysis indicates that this alternative does not likely warrant further evaluation.
<p>Air Conditioning (cold trap)</p>	<p>Reduce absolute humidity of extracted soil vapor to prevent tritiated water from contacting GAC. A refrigerative dryer would be installed upstream of the GAC to remove water vapor. HTO condensate would be collected, passed through GAC, and injected to the subsurface.</p>	<ul style="list-style-type: none"> • Allows the vapor stream to be treated economically by GAC without producing a mixed waste stream. • Proven technology to dry air. • Relatively low cost. 	<ul style="list-style-type: none"> • It is anticipated that sufficient VOCs would likely remain in the condensed water to require further treatment of the condensate to remove the VOCs. The removal of the VOCs (e.g., using GAC) could produce a mixed waste. 	<ul style="list-style-type: none"> • Need to determine dew point at which adsorption of HTO onto GAC in the vapor phase will be prevented.

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Desiccants	Install a molecular sieve with regeneration system to remove tritiated water from vapor stream prior to VOC treatment. Other disposable desiccants could also be used.	<ul style="list-style-type: none"> Allows the vapor stream to be treated economically by GAC without producing a mixed waste. 	<ul style="list-style-type: none"> Desiccant material may be mixed waste when disposed. If a disposable desiccant is used, it would need to be disposed of as a low level radioactive waste or flushed to remove tritium. Tests would need to be run to determine effectiveness. Not a proven technology for this application. 	<ul style="list-style-type: none"> Drierite, silica gel, calcium sulfate, calcium chloride, montmorillonite clay, and molecular sieves are commonly used as desiccants.
New Vapor Process VTF5475				
Ex Situ Catalytic Oxidation	Install a catalytic oxidation system to oxidize VOCs at low reaction temperatures (mostly 400-800°F) using metal catalyst. The addition of a catalyst to the basic thermal oxidation configuration can accelerate the rate of oxidation at relatively lower temperature by sorbing the oxygen from the air stream and the contaminant vapor onto the catalyst surface where they react to form carbon dioxide, water, and hydrochloric gas.	<ul style="list-style-type: none"> No chlorinated hydrocarbon waste. With proper selection of catalyst, operating conditions, and equipment design, catalytic oxidation can attain VOC destructions of up to 99%. Technology destroys VOCs, 	<ul style="list-style-type: none"> Potentially high cost. High energy consumption for temperature increase, may require added protections. Release of acidic vapor, needing additional treatment. O&M issues remain. Catalyst needs to be replaced. Formation of dioxins and furans is a concern. 	<ul style="list-style-type: none"> Possible catalysts used for oxidation <ul style="list-style-type: none"> Palladium Platinum Rhodium Metal oxides (nickel oxide, copper oxide, manganese dioxide, or chromium oxide) Alumina supported cobalt oxide system (CoO_x/Al₂O₃) Preliminary analysis indicates that this alternative does not likely warrant further evaluation.
Membrane Separation	In this process, VOC-laden air contacts one side of a membrane that is permeable to organic vapors but relatively impermeable to air. A partial vacuum, applied to the other side, draws the organic vapor through the membrane. The permeate vapor is then compressed and condensed to recover the organic fraction. Membranes are typically made of a polymer, and are designed for each application. Vapor separation occurs due to difference in solubility; the membrane allows larger hydrocarbon molecules to permeate faster through the membrane polymer compared to smaller molecules such as nitrogen, hydrogen, and oxygen.	<ul style="list-style-type: none"> Can achieve high recovery efficiencies when combined with condensation (>90%) without operating at cryogenic temperatures. Can allow efficient recovery of high volatility (low boiling point) VOCs. 	<ul style="list-style-type: none"> High O&M activities and costs due to potential fouling of membranes. Typically used at higher concentrations of VOCs (mostly >100 ppmv) and low flow rates. The VOC stream that passes through the polymer membrane can also contain moisture (tritium). New technology with little field implementation knowledge. Not a proven technology for this application. 	<ul style="list-style-type: none"> Membranes (from literature) include: <ul style="list-style-type: none"> Composite polymer membrane Dense elastomeric silicone on top of a porous polyether-imide or polyvinylidene-fluoride support. Nonporous nanofiltration membranes Liquid membrane of triethylene glycol No information on behavior of these membranes for tritium. Preliminary analysis indicates that this alternative does not likely warrant further evaluation.
New Treatment Process – In Situ				
In-situ Chemical Reductive Dehalogenation	A chemical such as Zero Valent Iron (ZVI) or Ferox SM is added to the subsurface as an abiotic electron donor to promote the reductive dehalogenation of the chlorinated VOCs. Atomized slurry is injected into injection wells. The slurry is prepared using potable water and ZVI powder and fed into a high flow, high-velocity nitrogen gas or compressed air stream. The ZVI slurry is thereby atomized into an aerosol with characteristics more closely resembling that of a gas instead of an incompressible fluid.	<ul style="list-style-type: none"> Potentially effective source area treatment. If successful, shorter time to achieve VOC remediation goals. No generated waste. Technology destroys VOCs, 	<ul style="list-style-type: none"> Bench and pilot scale tests required. 	<ul style="list-style-type: none"> Method can be used in combination with plume control or as subsurface VOC remediation without plume control. Depth to groundwater (bgs): CRD-1 (138 ft), CRD-2 (155-175 ft), TF518-N (208 ft). Inorganic field parameters such as dissolved oxygen (DO), Oxidation-Reduction Potential (ORP), Temp, pH, sulfate, sulfide, nitrate need to be determined. Flow parameters such as porosity, permeability, flow rate and direction of groundwater are important in the design of a system. An estimate of the plume size and shape for each site needs to be made to determine the amount and location of injections.

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<p><i>In-situ Chemical Oxidation</i></p>	<p>Subsurface delivery of chemical oxidants to contaminated media in order to destroy the contaminants by converting them to innocuous compounds. The oxidant can be delivered to the subsurface through injection or sparging wells. The oxidants applied in this process are typically hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), ozone, or Fenton's Reagent (H₂O₂ and iron catalyst).</p>	<ul style="list-style-type: none"> • Potentially effective source area treatment. If successful, shorter time to achieve VOC remediation goals. • No generated waste. • Technology destroys VOCs, 	<ul style="list-style-type: none"> • Potential to oxidize metals. • Possible mobilization of trace metals. • Destroys subsurface microbial population. • Bench and pilot scale tests required. • Handling of hazardous material (oxidants). 	<ul style="list-style-type: none"> • Method can be used in combination with plume control or as subsurface VOC remediation without plume control. • Preliminary analysis indicates that this alternative does not likely warrant further evaluation.
<p><i>In-situ Biological Reductive Dehalogenation</i></p>	<p>Bioaugmentation involves stimulating indigenous microbial cultures by adding nutrients to encourage reductive dehalogenation. Nutrients commonly injected include edible oils, cheese whey, molasses, sodium lactate, emulsified vegetable oil and/ or proprietary nutrients such as HRC (a proprietary polylactate ester).</p> <p>Bioaugmentation involves addition of microorganisms (such as <i>Dehalococcoides ethenogenes</i>, <i>Dehalosporillum multivorans</i>, <i>Dehalobacter restrictus</i>) to the subsurface to enhance the existing microbial community. This is followed by the addition of nutrients to encourage reductive dehalogenation.</p>	<ul style="list-style-type: none"> • Potentially effective source area treatment. If successful, shorter time to achieve VOC remediation goals. • No generated waste. • Microcosm studies for TFD Helipad area showed successful reductive dehalogenation of TCE by adding lactate or emulsified vegetable oil. • Technology destroys VOCs, 	<ul style="list-style-type: none"> • Bench and pilot scale tests required. 	<ul style="list-style-type: none"> • Method can be used in combination with plume control or as subsurface VOC remediation without plume control. • This technology will be evaluated in detail based on the results of the Enhanced Source Area Remediation (ESAR) project at TFD Helipad.